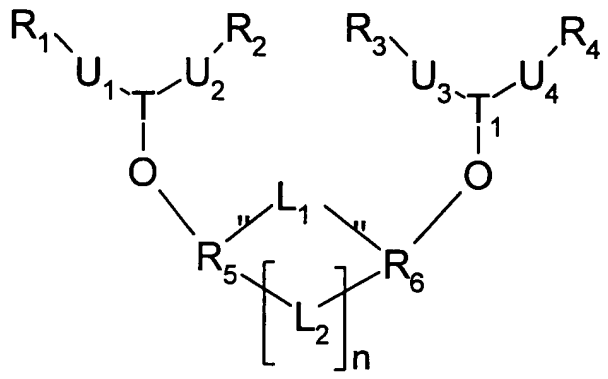
CLAIMS

1. Process for hydrocyanating a hydrocarbon compound containing at least one ethylenic unsaturation by reacting it in a liquid medium with hydrogen cyanide in the presence of a catalyst comprising a metallic element selected from transition metals and an organic ligand, characterized in that the organic ligand corresponds to the general formula I below:



(I)

in which:

T and T_1, which are identical or different, represent a phosphorus, arsenic or antimony atom,

R_1, R_2, R_3 and R_4, which are identical or different, represent a substituted or unsubstituted, aromatic, aliphatic or cycloaliphatic radical comprising one or more rings, which are in fused form or not and which may contain one or more heteroatoms, where the radicals R_1 and R_2 on the one hand and R_3 and R_4 on the other hand may be interconnected by a covalent bond, a hydrocarbon chain or a heteroatom,

U_1, U_2, U_3 and U_4, which are identical or different, represent an oxygen atom or a radical of formula NR in which R denotes a monovalent alkyl, aryl, cycloalkyl, sulphonyl or carbonyl radical,

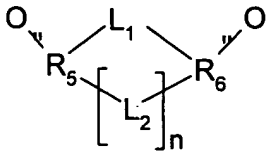
R_5 and R_6, which are identical or different, represent an aryl or cycloaliphatic group which may comprise heteroatoms and/or one or more rings, in fused form or not, and which are substituted or unsubstituted,

n is an integer equal to 0 or 1,

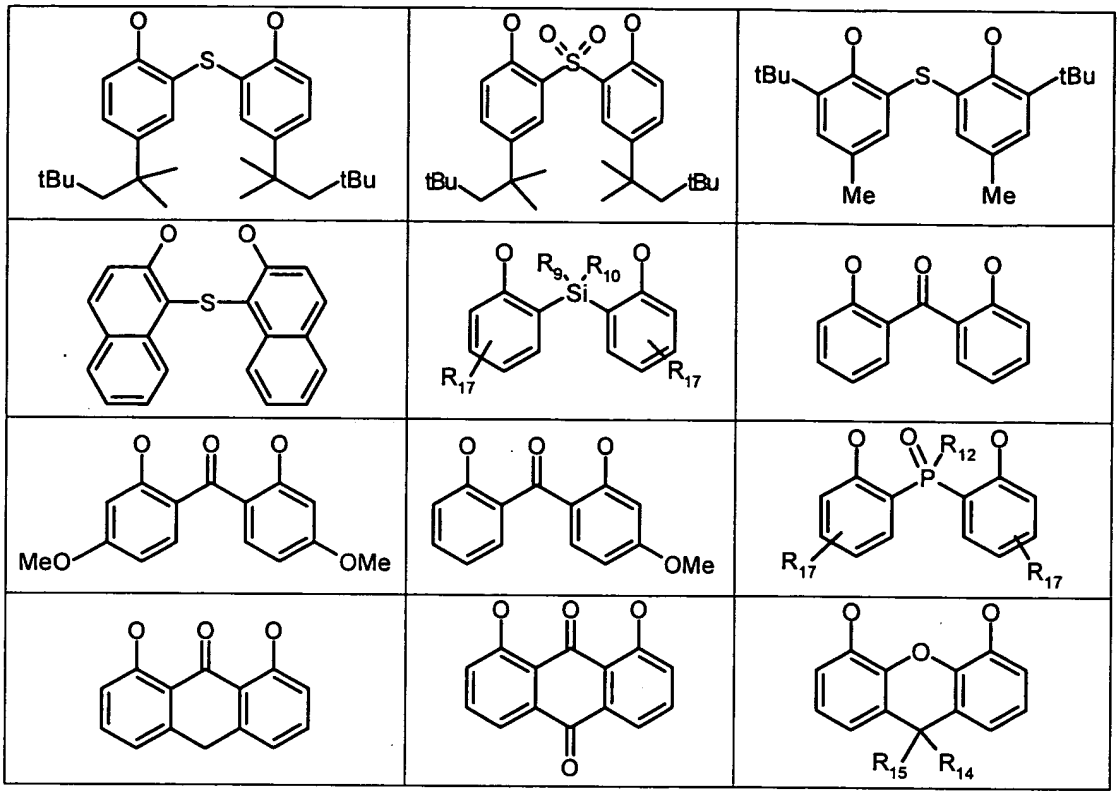
L_1, when n is 0, represents a divalent radical selected from the group consisting of the groups NR_7, PR_8, SiR_9R_{10}, BR_{11}, S, POR_{12}, SO_2 and CO, in which R_7 is as defined for R above, R_8 and R_{12} may represent the radical OR_{13}, and R_8, R_9, R_{10}, R_{11}, R_{12} and R_{13} represent alkyl, aryl or cycloalkyl radicals,

L_1 and L_2, when n is 1, are identical or different and represent a covalent bond or a radical selected from the group consisting of the groups O, NR_7, PR_8, SiR_9R_{10}, BR_{11}, S, POR_{12}, SO_2, CO and $-CR_{14}R_{15}-$, in which R_7 is as defined for R above, R_8 and R_{12} may represent the radical OR_{13}, and R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} represent alkyl, aryl or cycloalkyl radicals, it being possible also for R_{14} and R_{15} to represent a hydrogen atom.

2. Process according to Claim 1, characterized in that the organic ligand of general formula I comprises a structure:

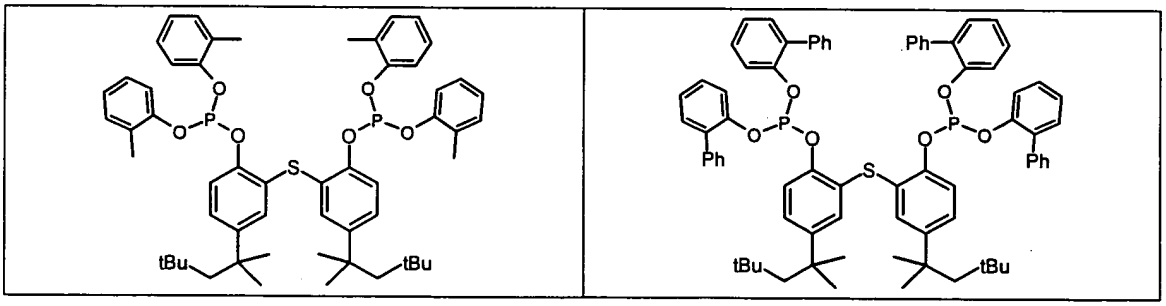


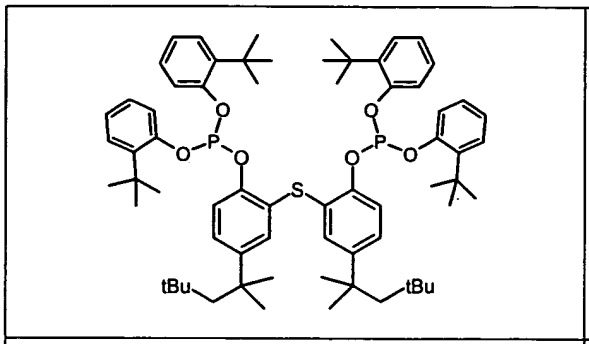
selected from the group consisting of the following structures:

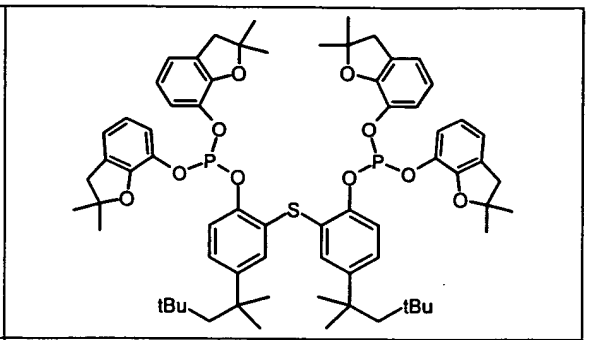


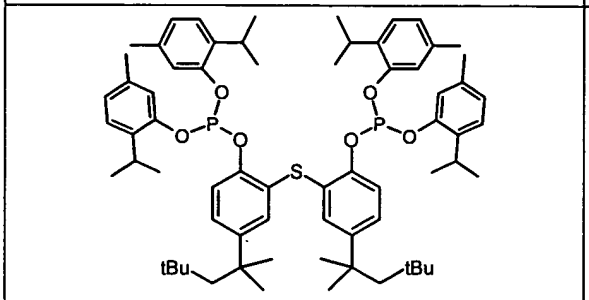
in which R_{17} represents an alkyl, aryl, halogen, alkoxy, thiol, cyano, nitro, aryloxy, alkoxycarbonyl, acyl or formyl radical.

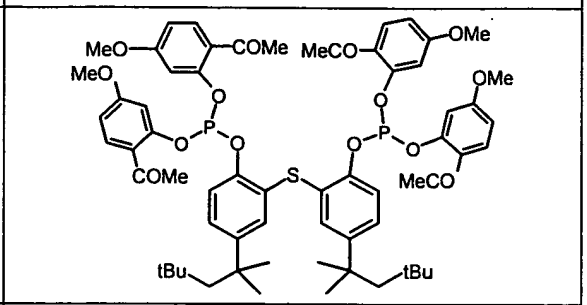
3. Process according to Claim 1 or 2, characterized in that the organic ligand of formula I is selected from the group consisting of:

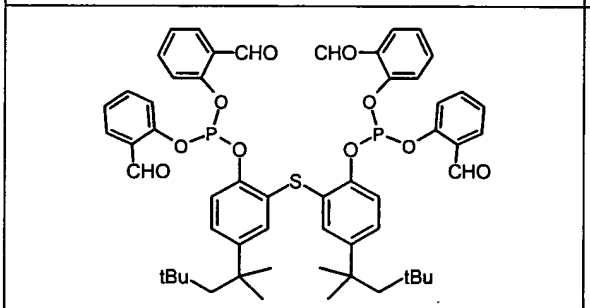


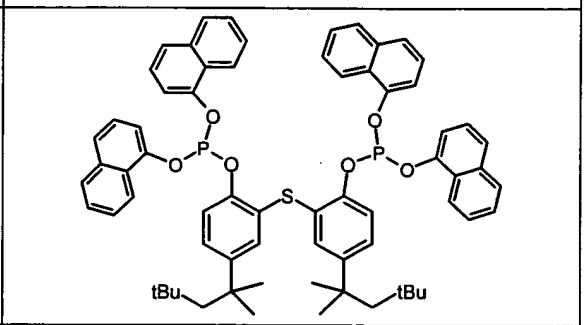


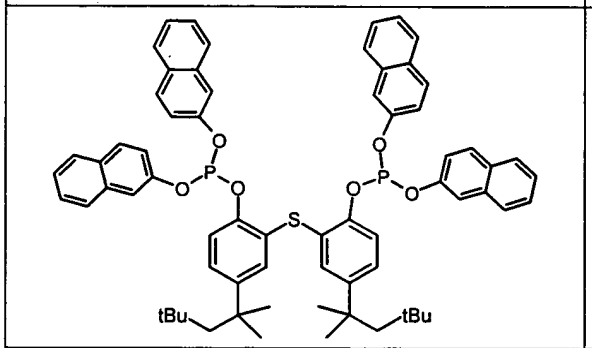


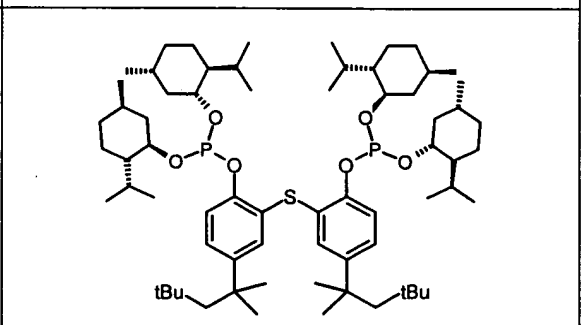


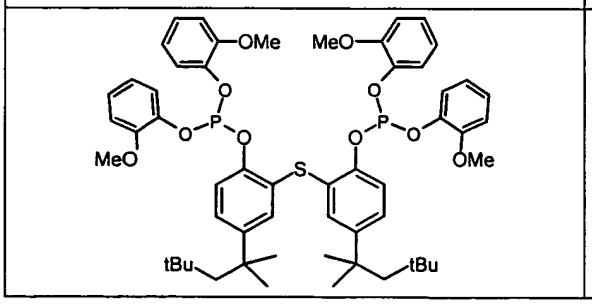


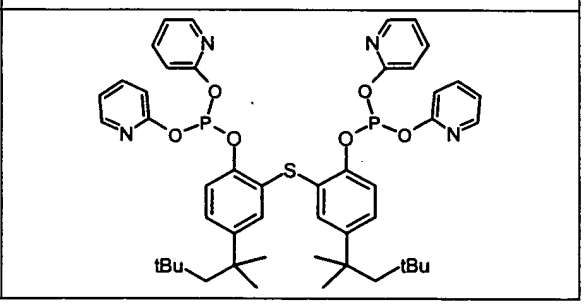


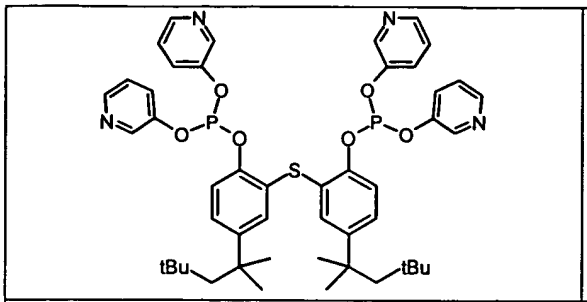
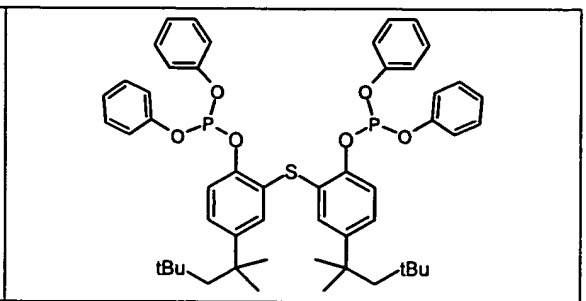
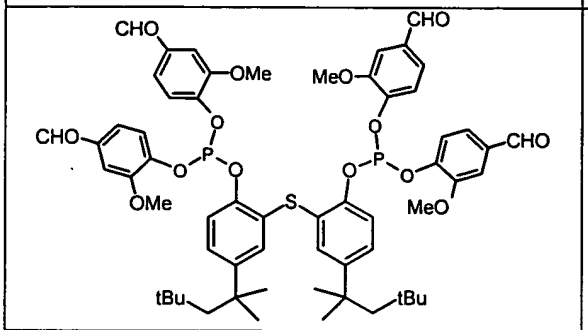
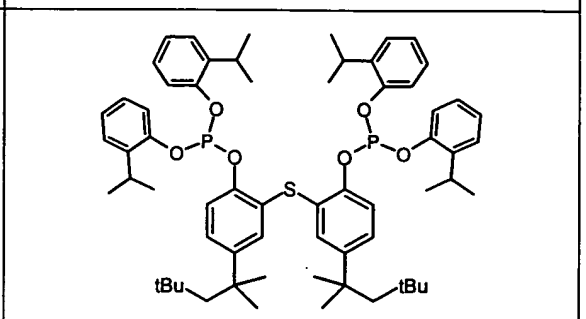
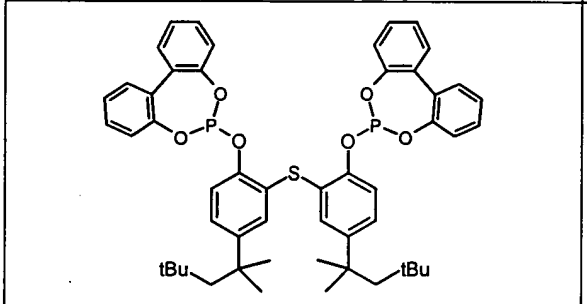
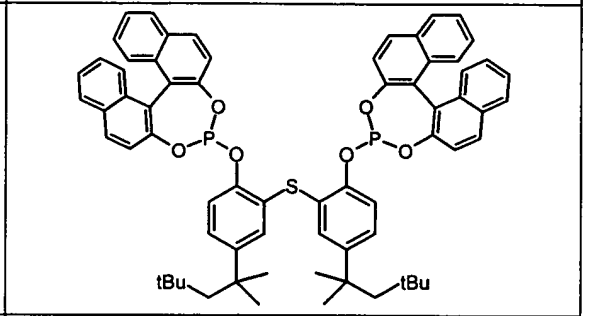
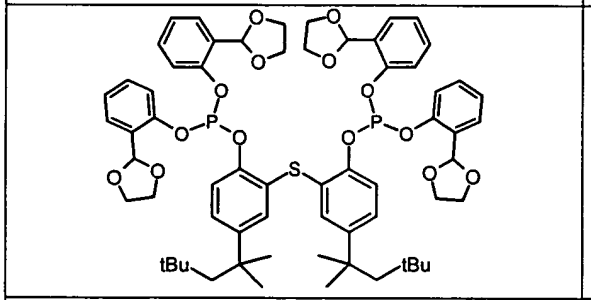
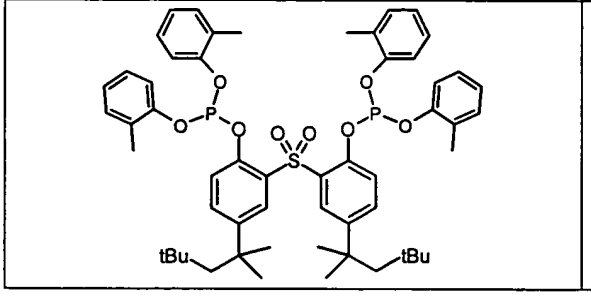


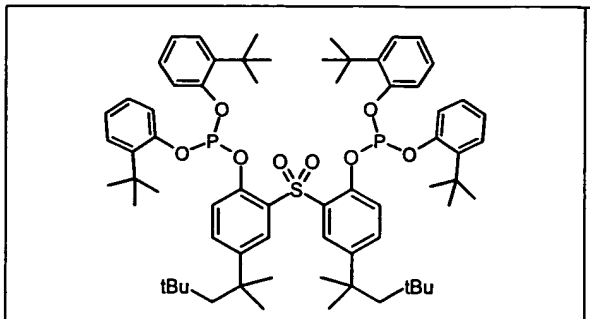






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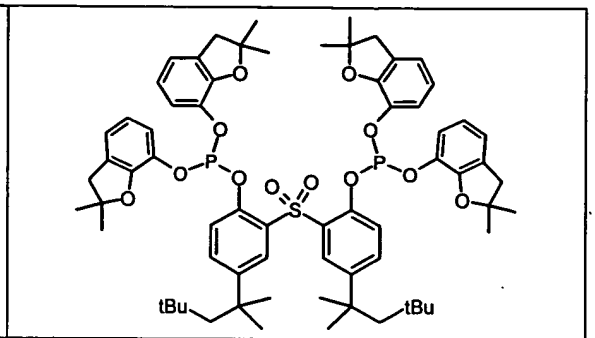
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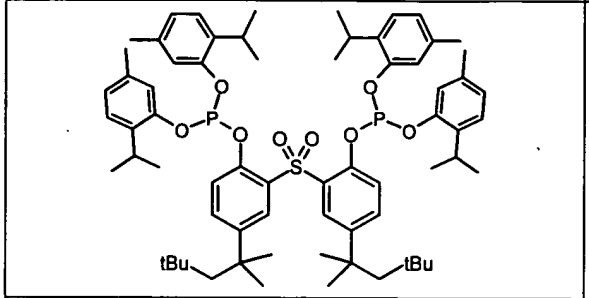
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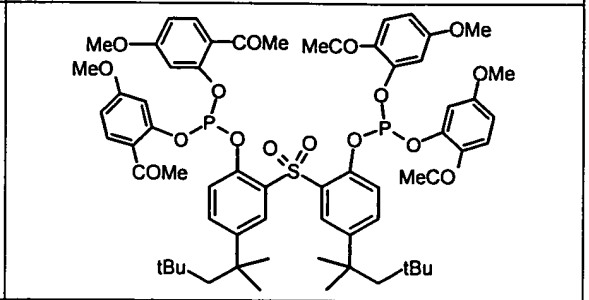
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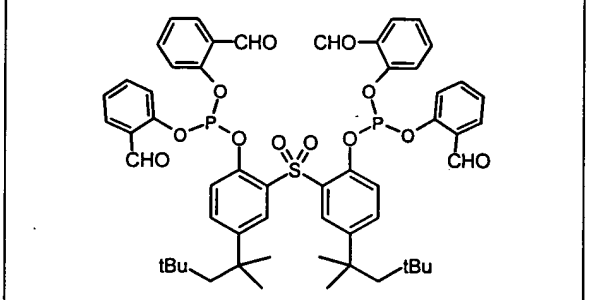
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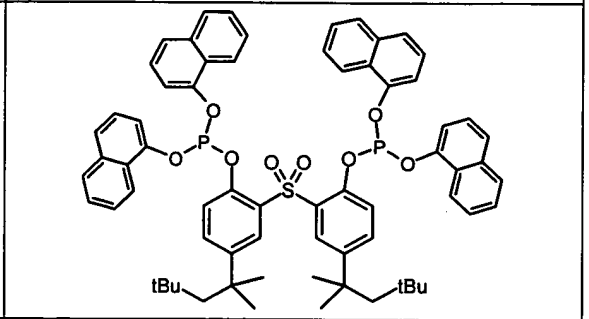
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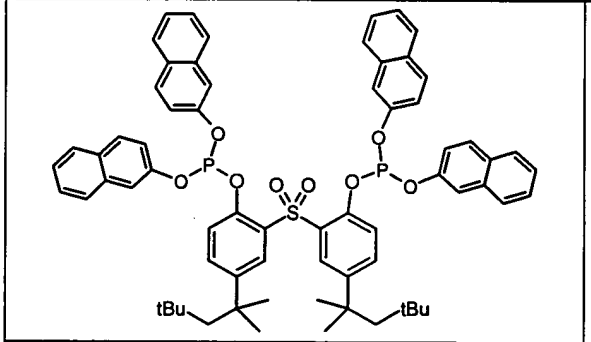
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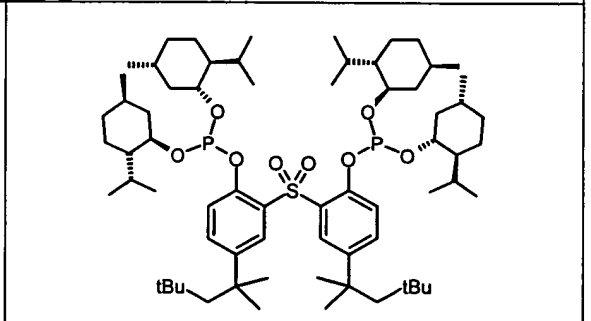
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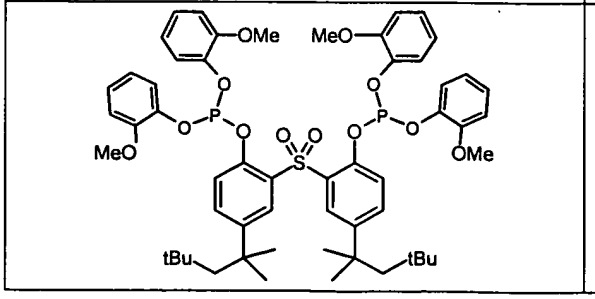
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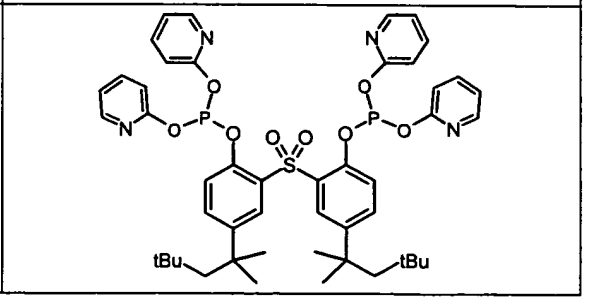
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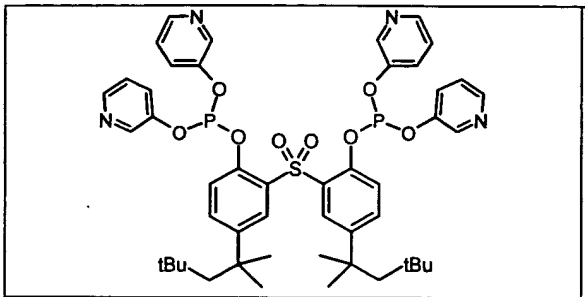

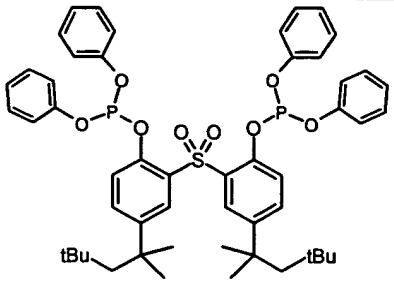

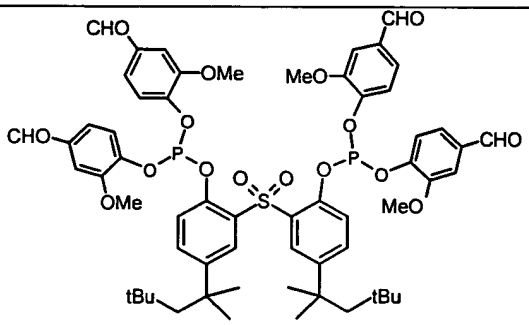

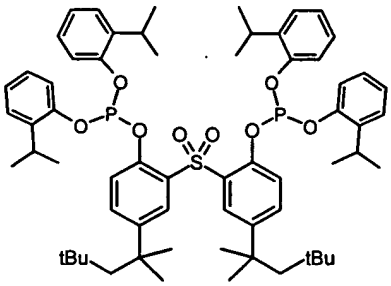

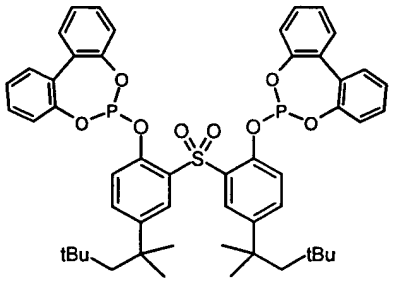

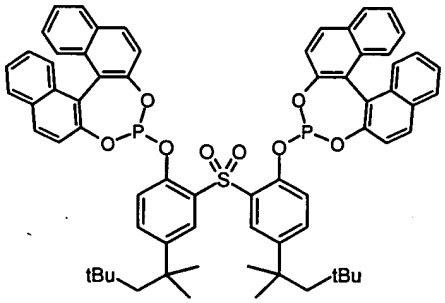

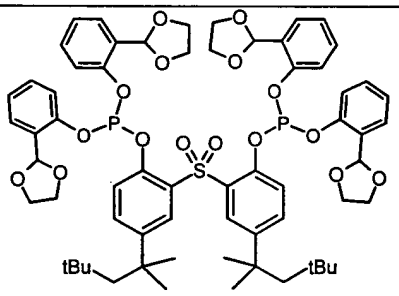

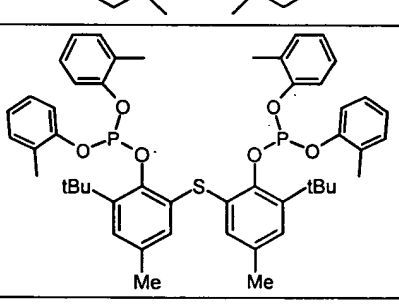

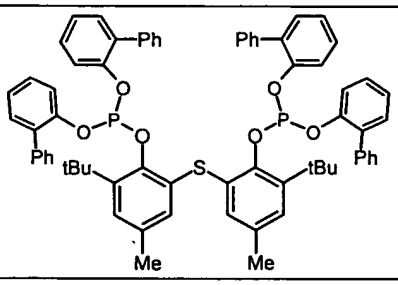

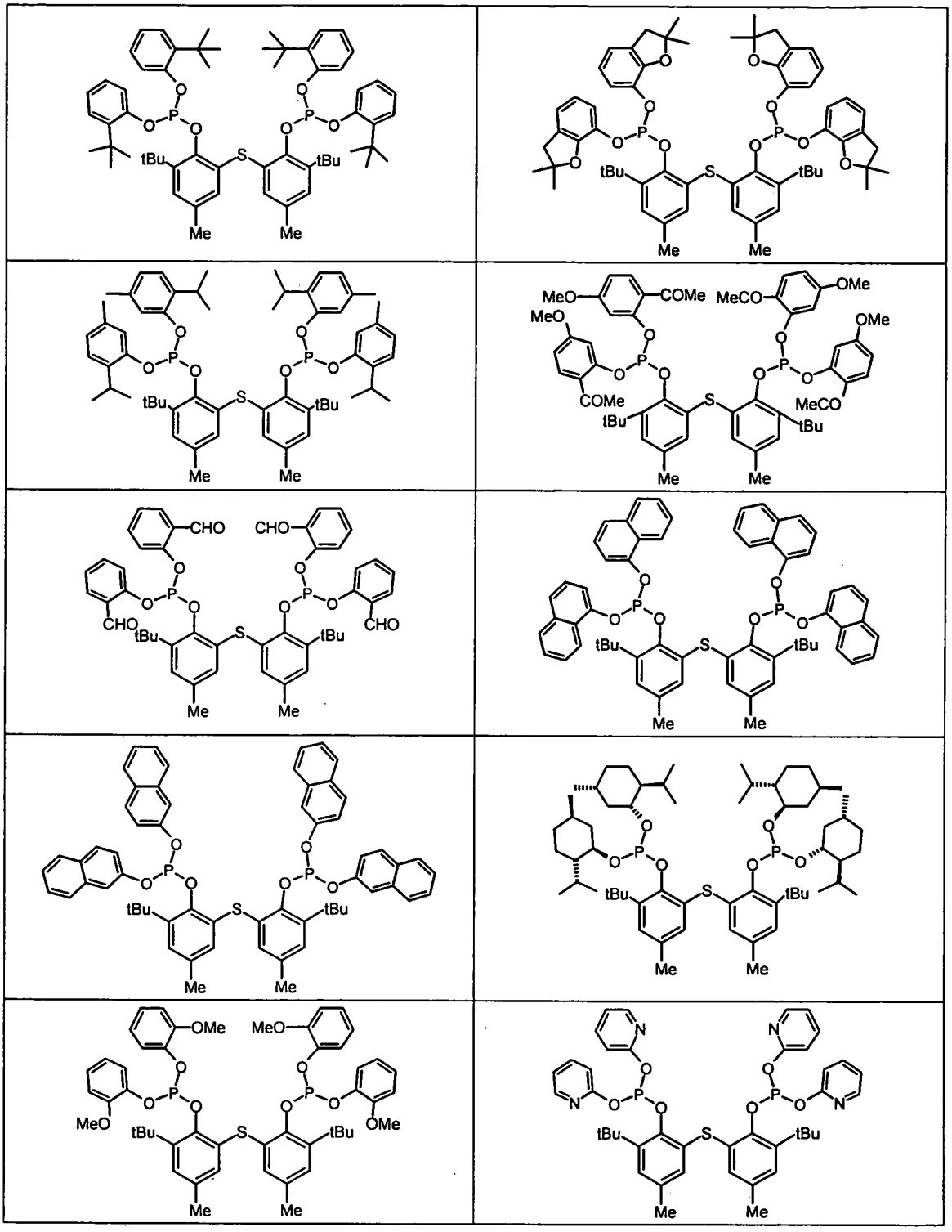

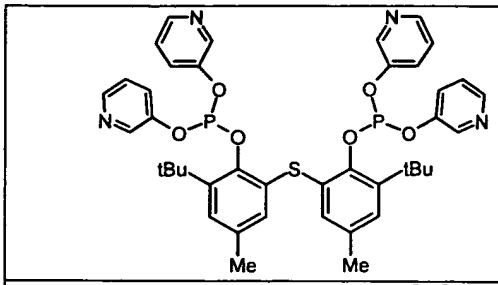
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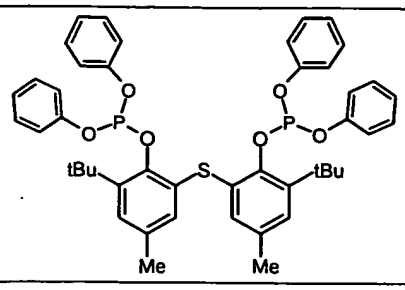
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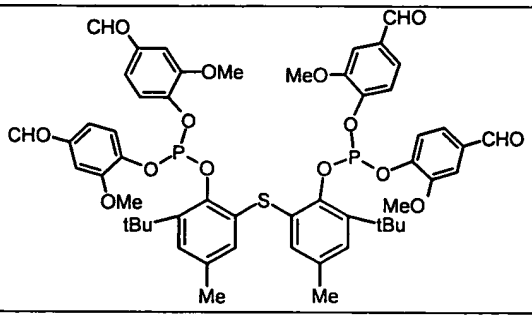
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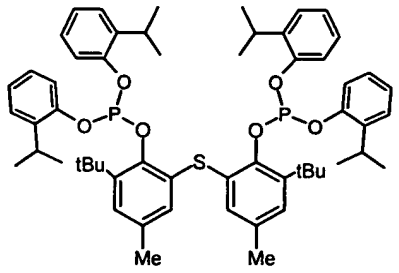
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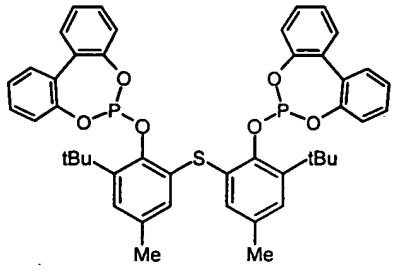
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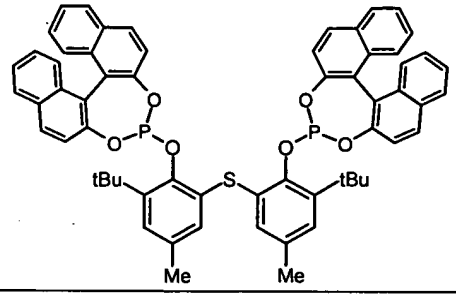
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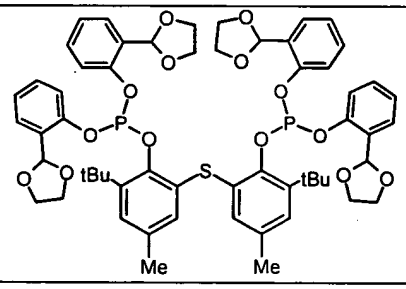
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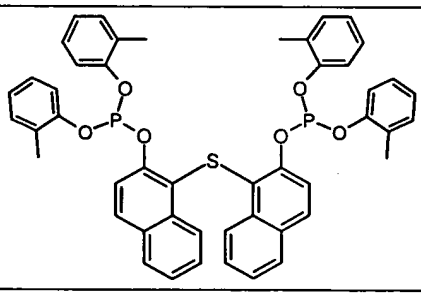
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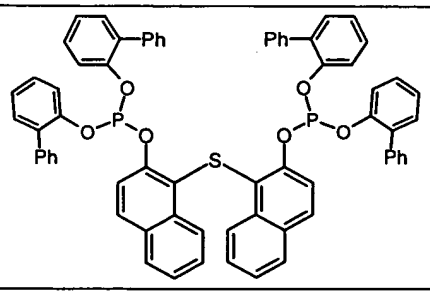
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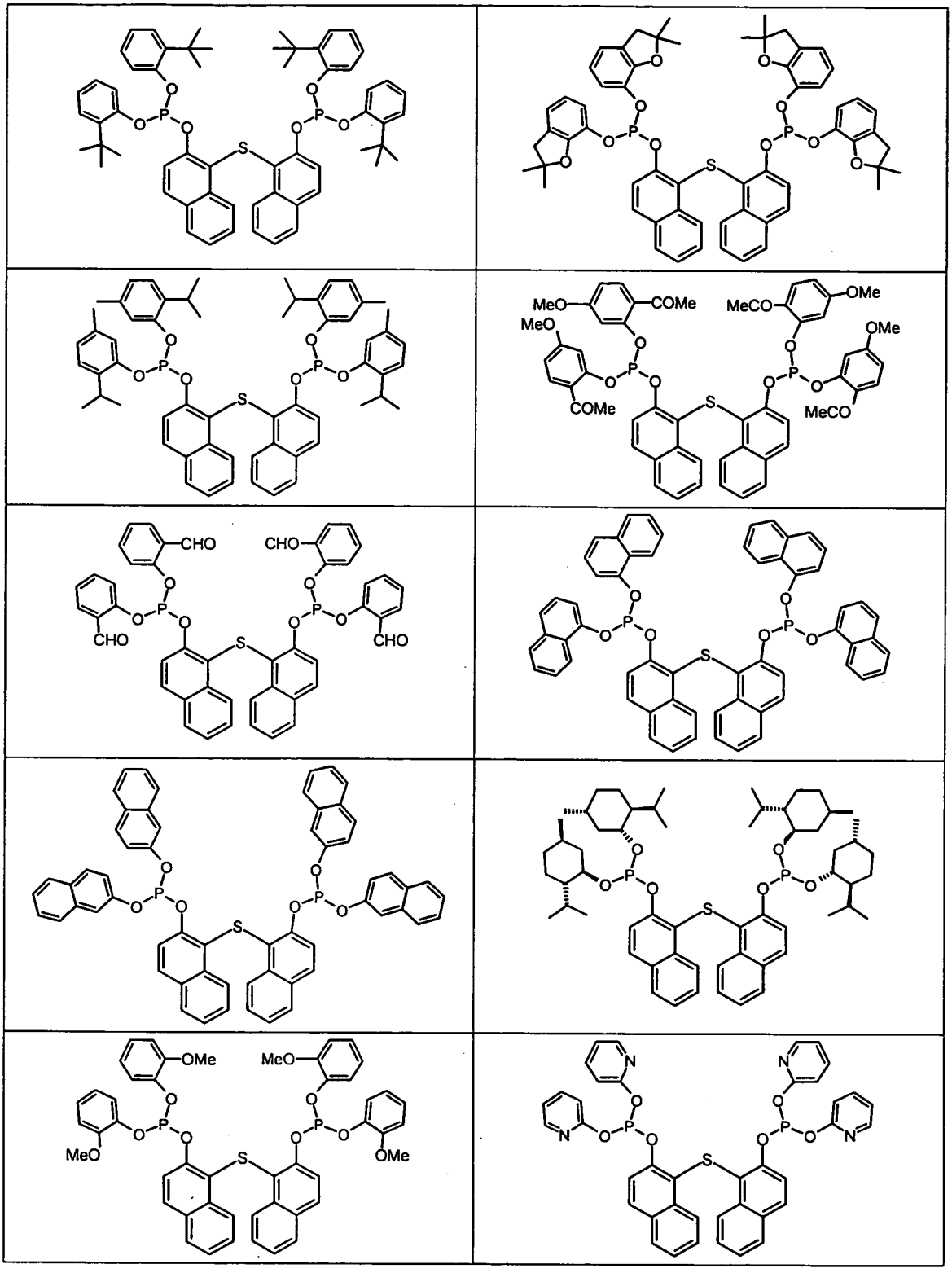
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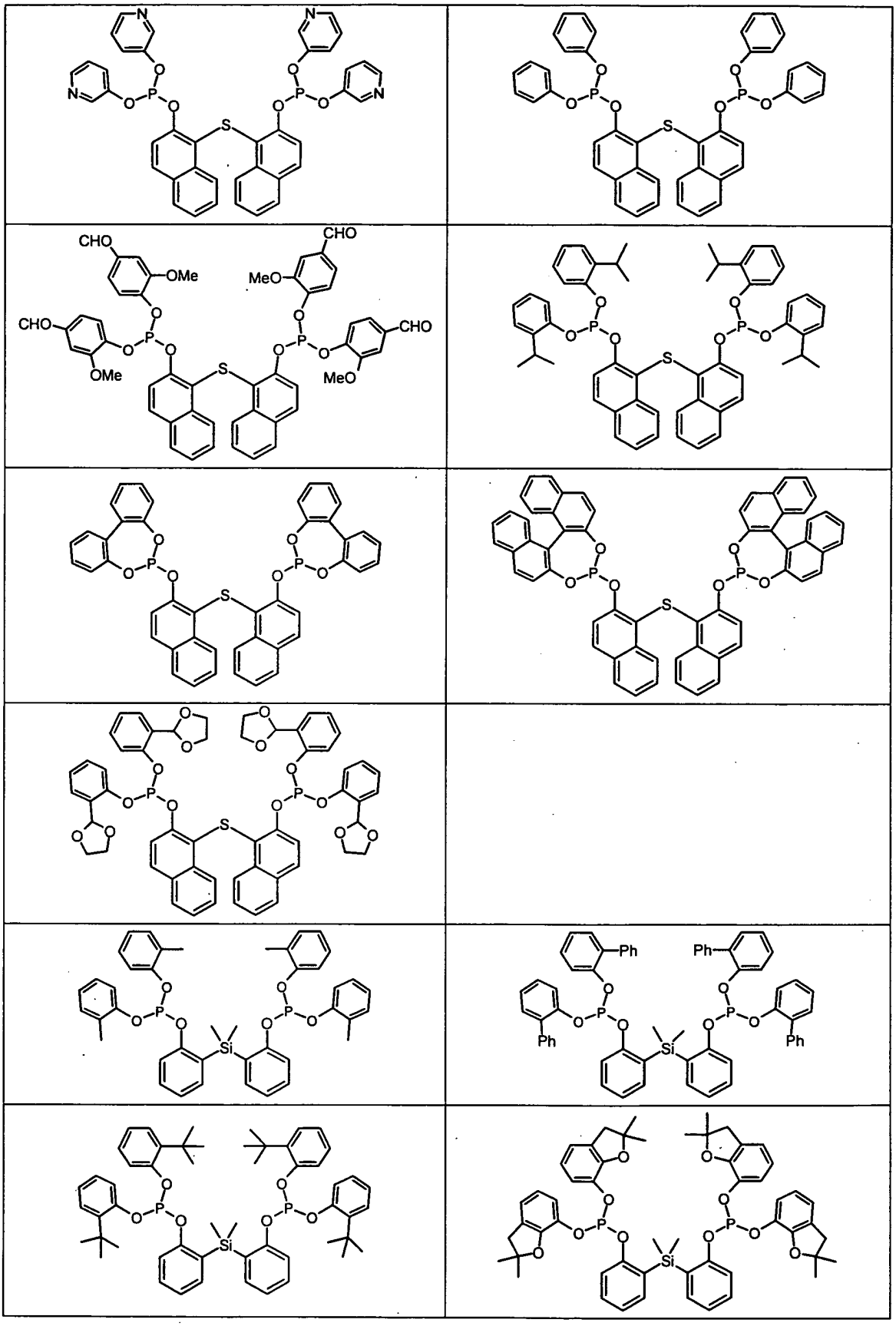

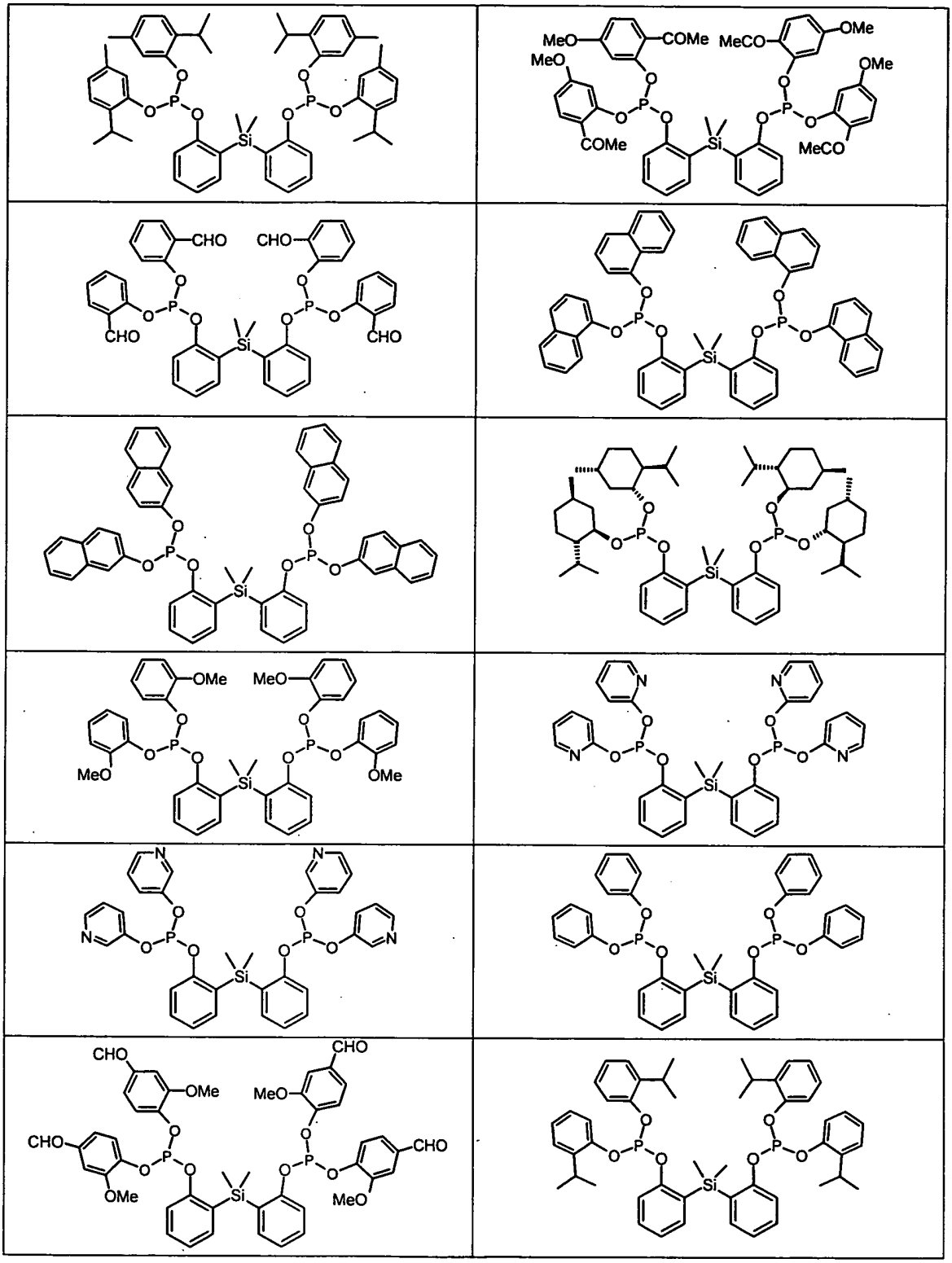

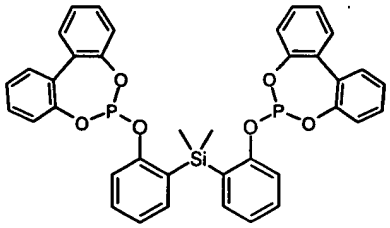	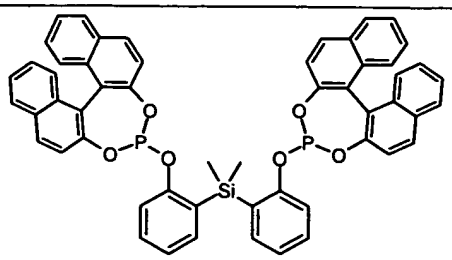
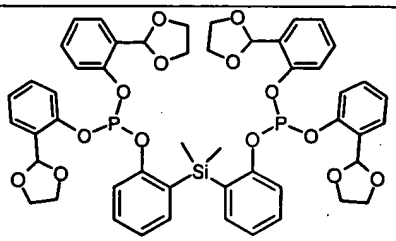	
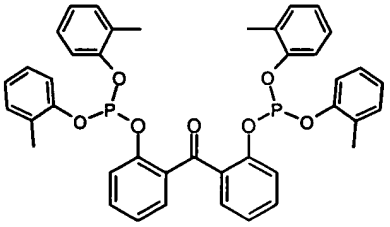	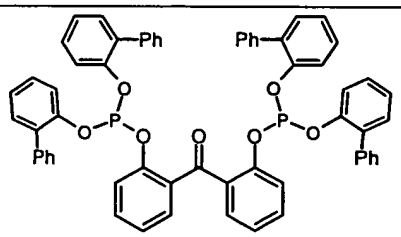
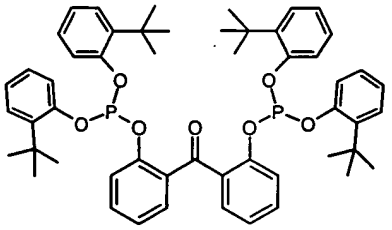	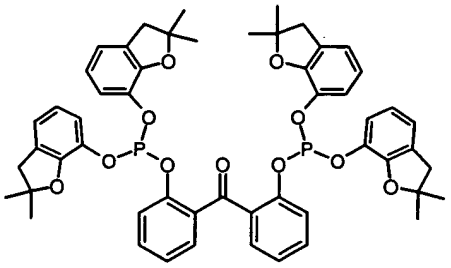
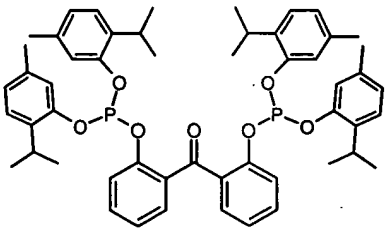	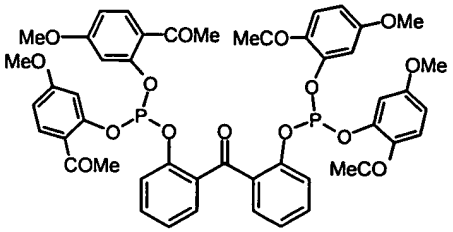
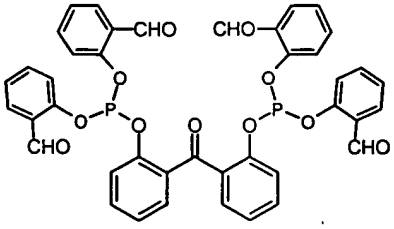	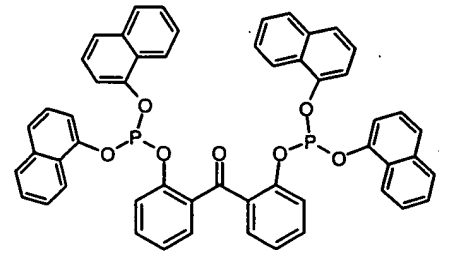

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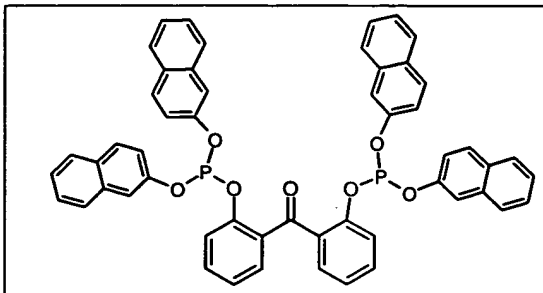

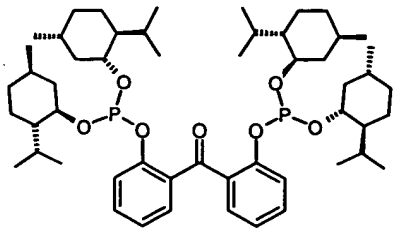

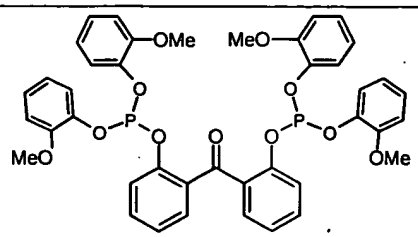
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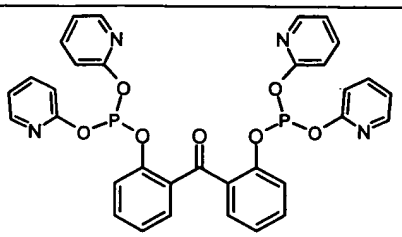
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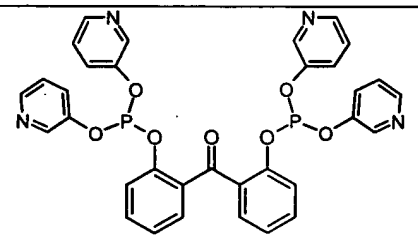
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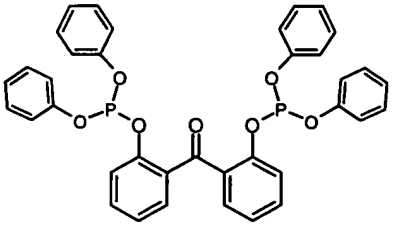

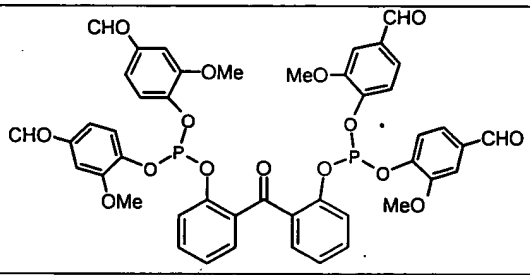
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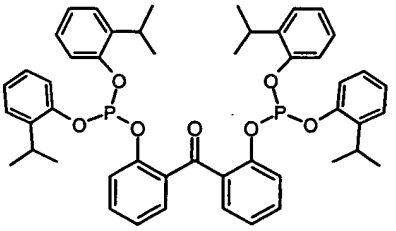

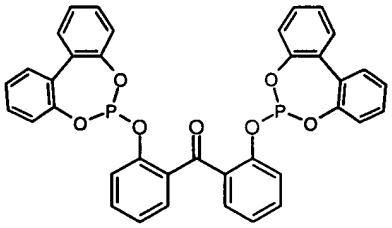

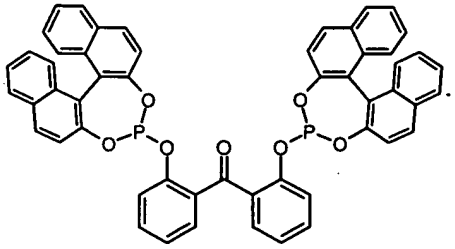

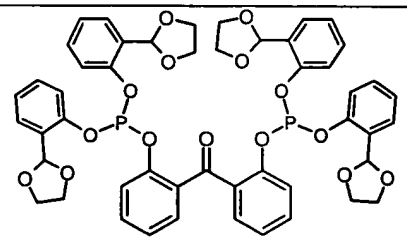

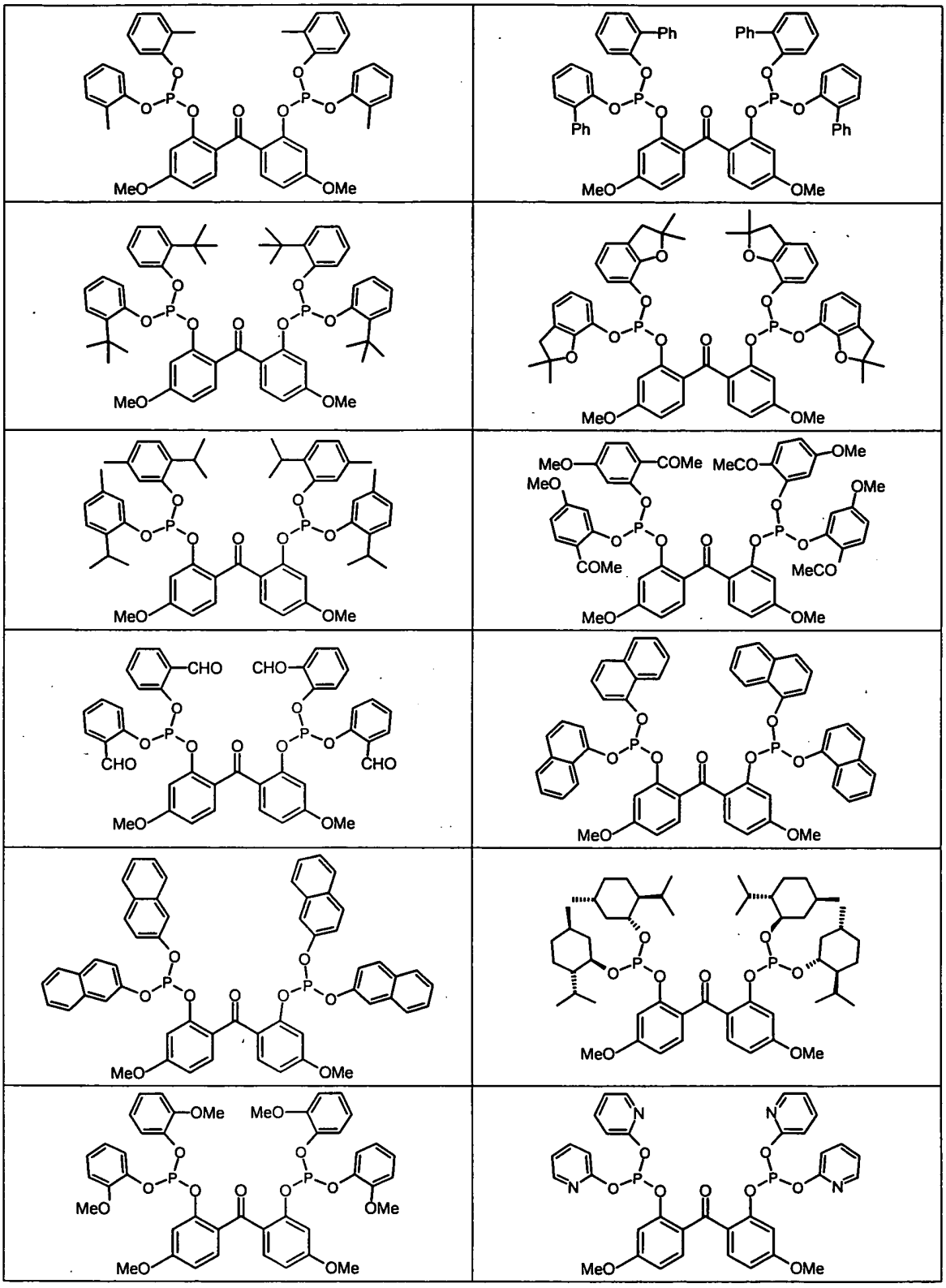
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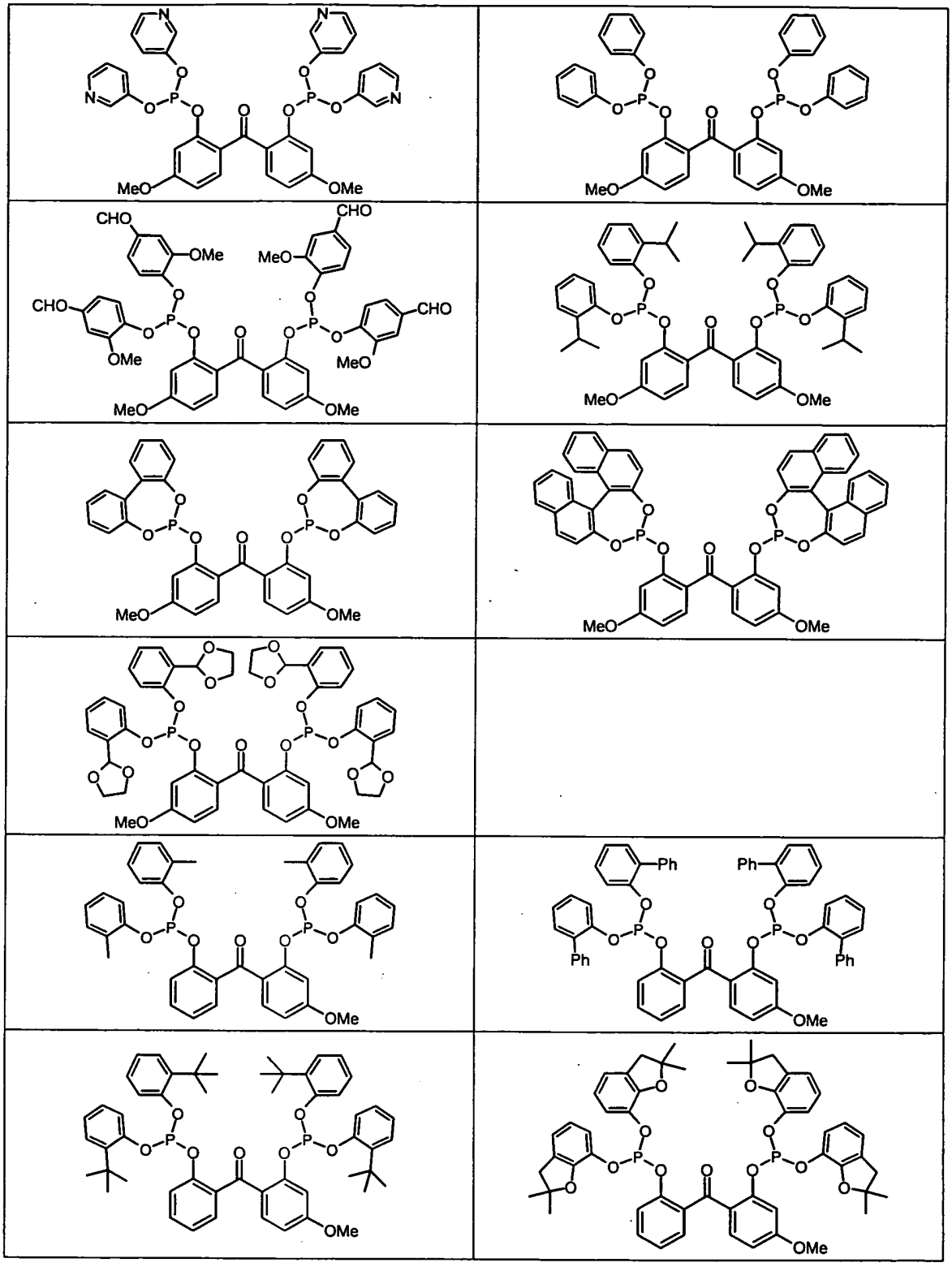

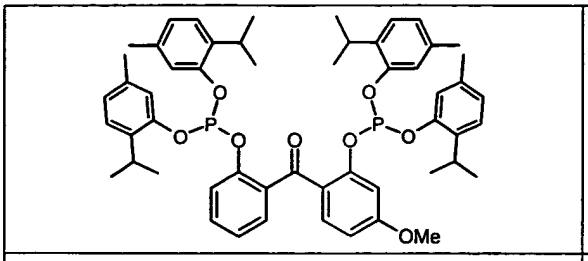
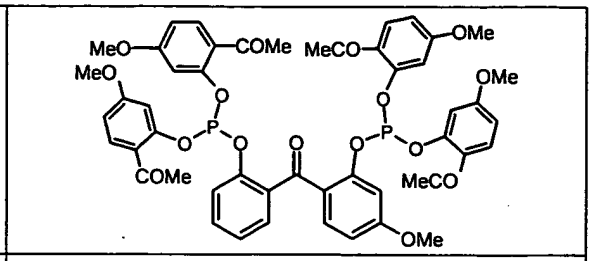
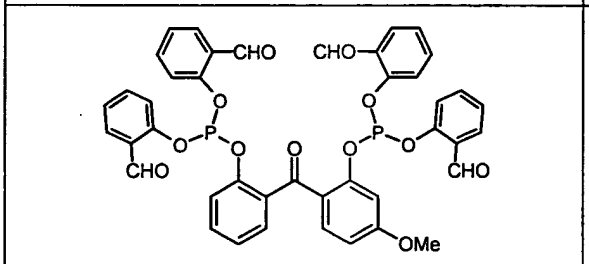
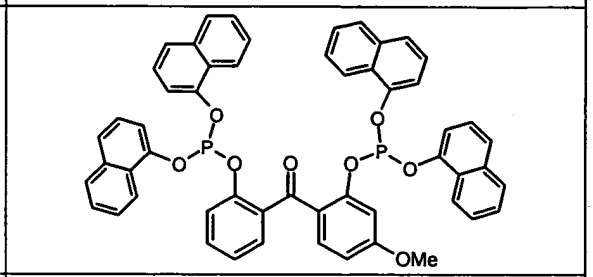
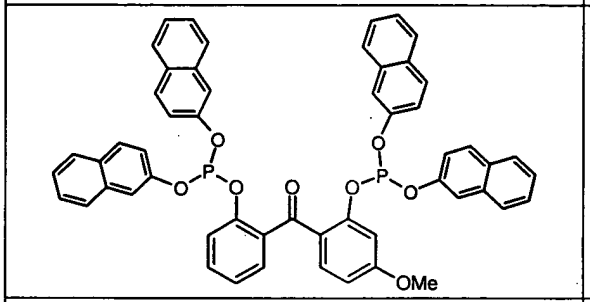
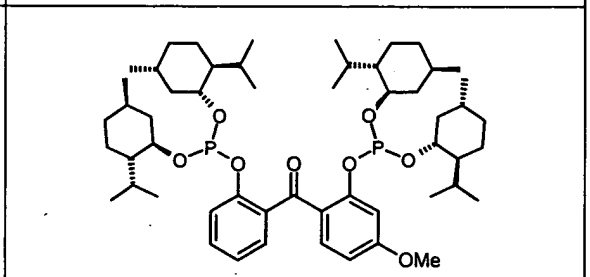
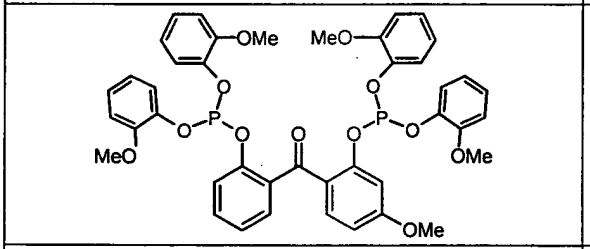
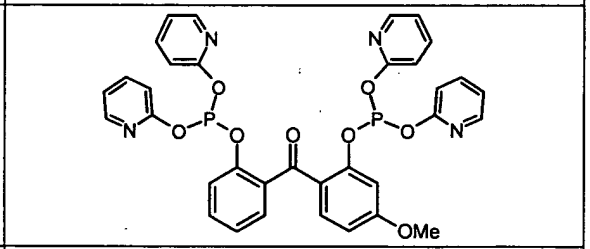
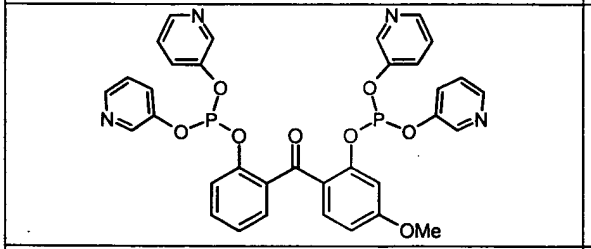
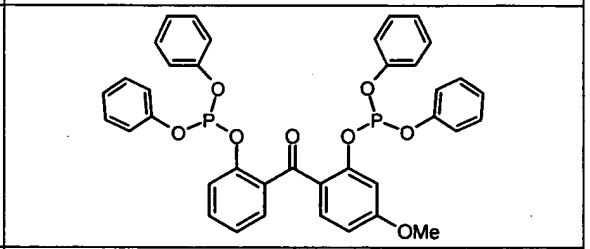
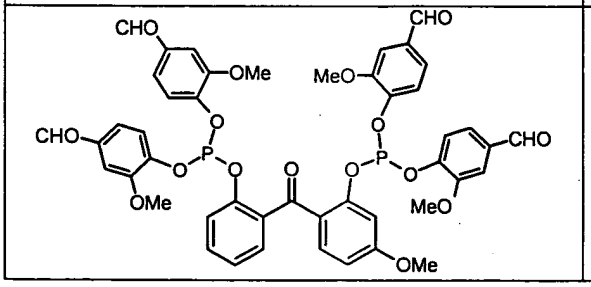
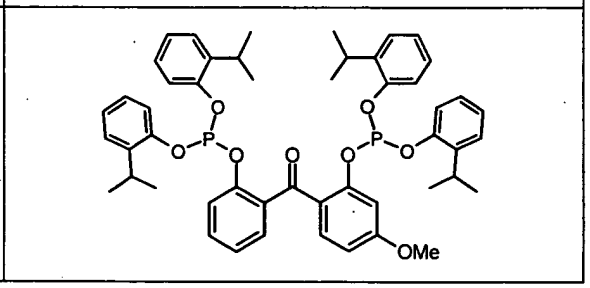
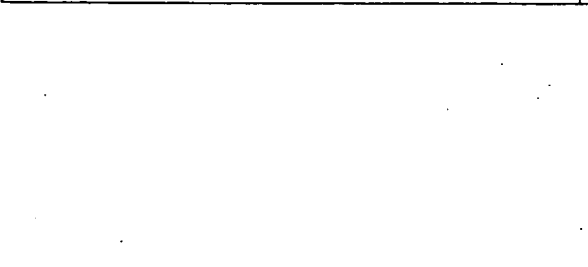
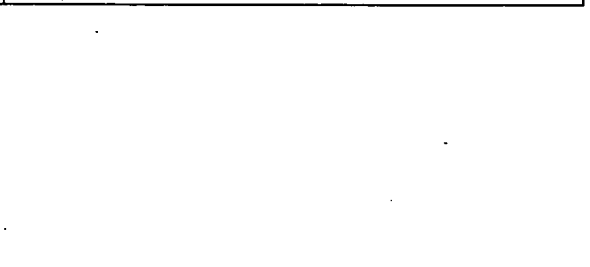

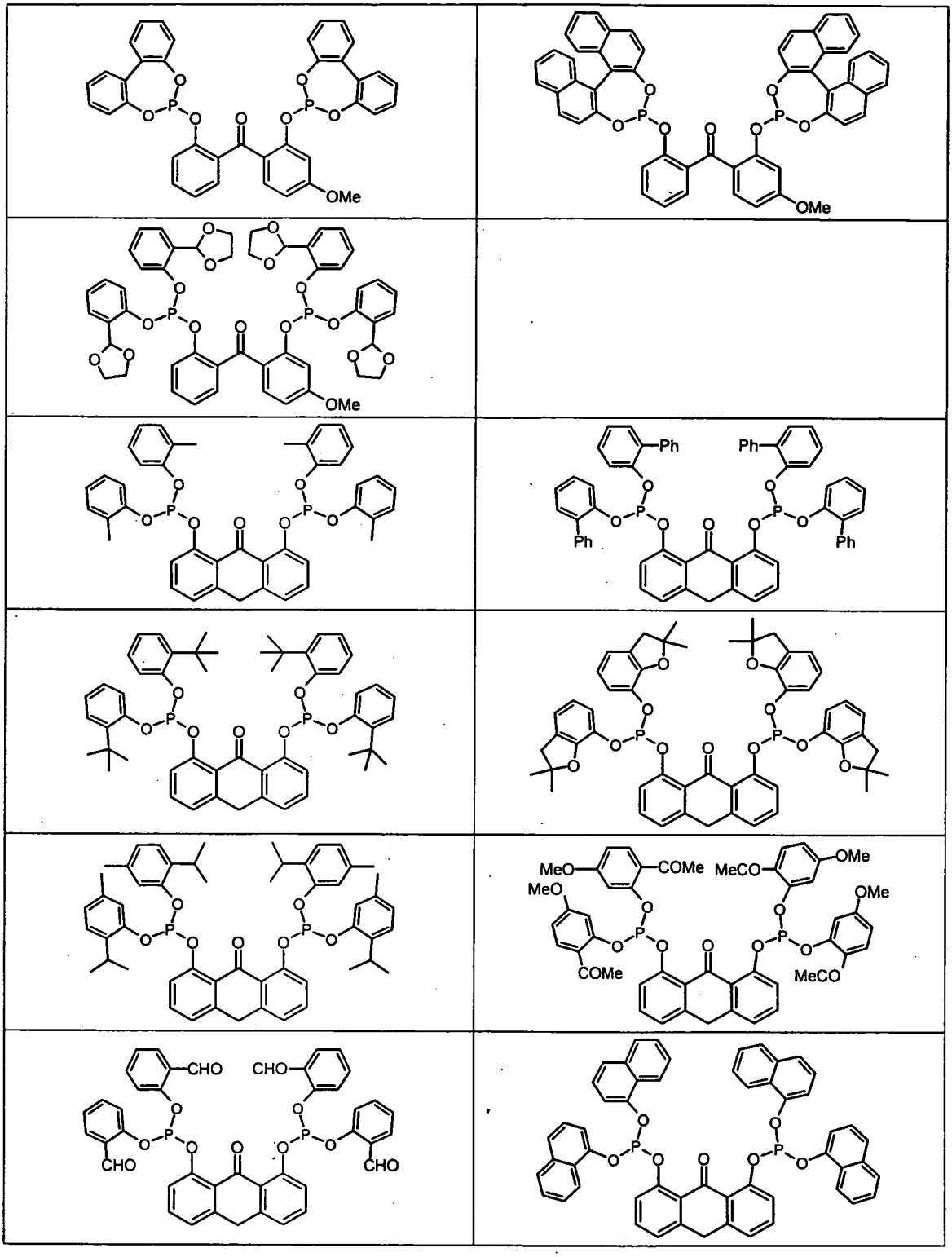
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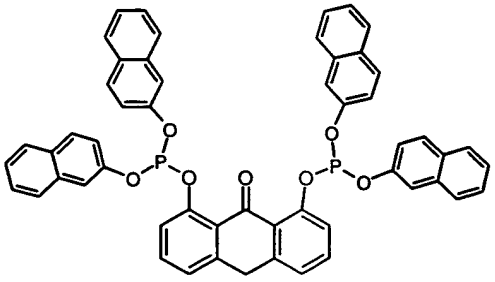

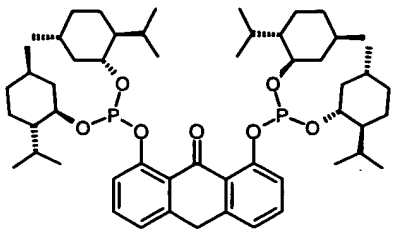

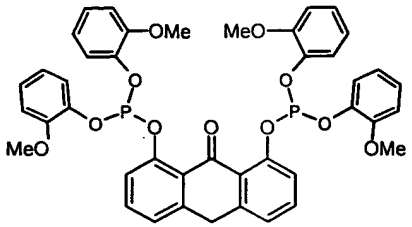

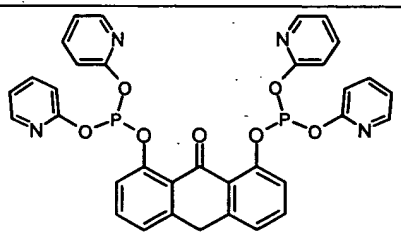

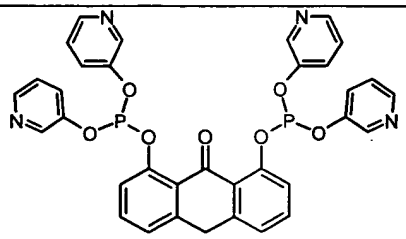

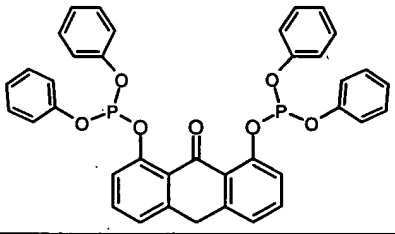

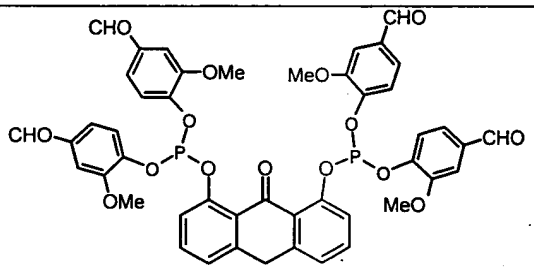

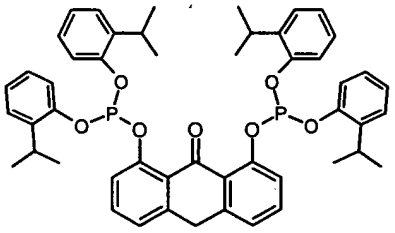

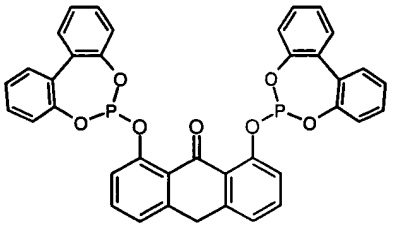

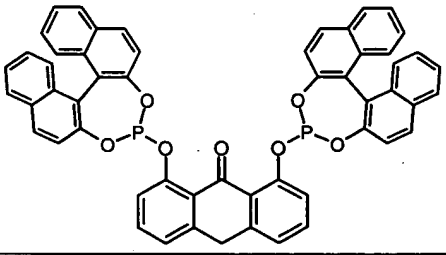

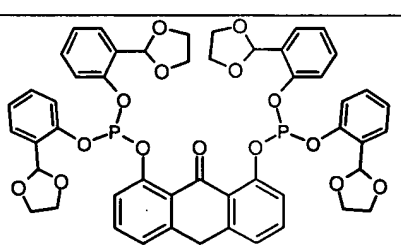

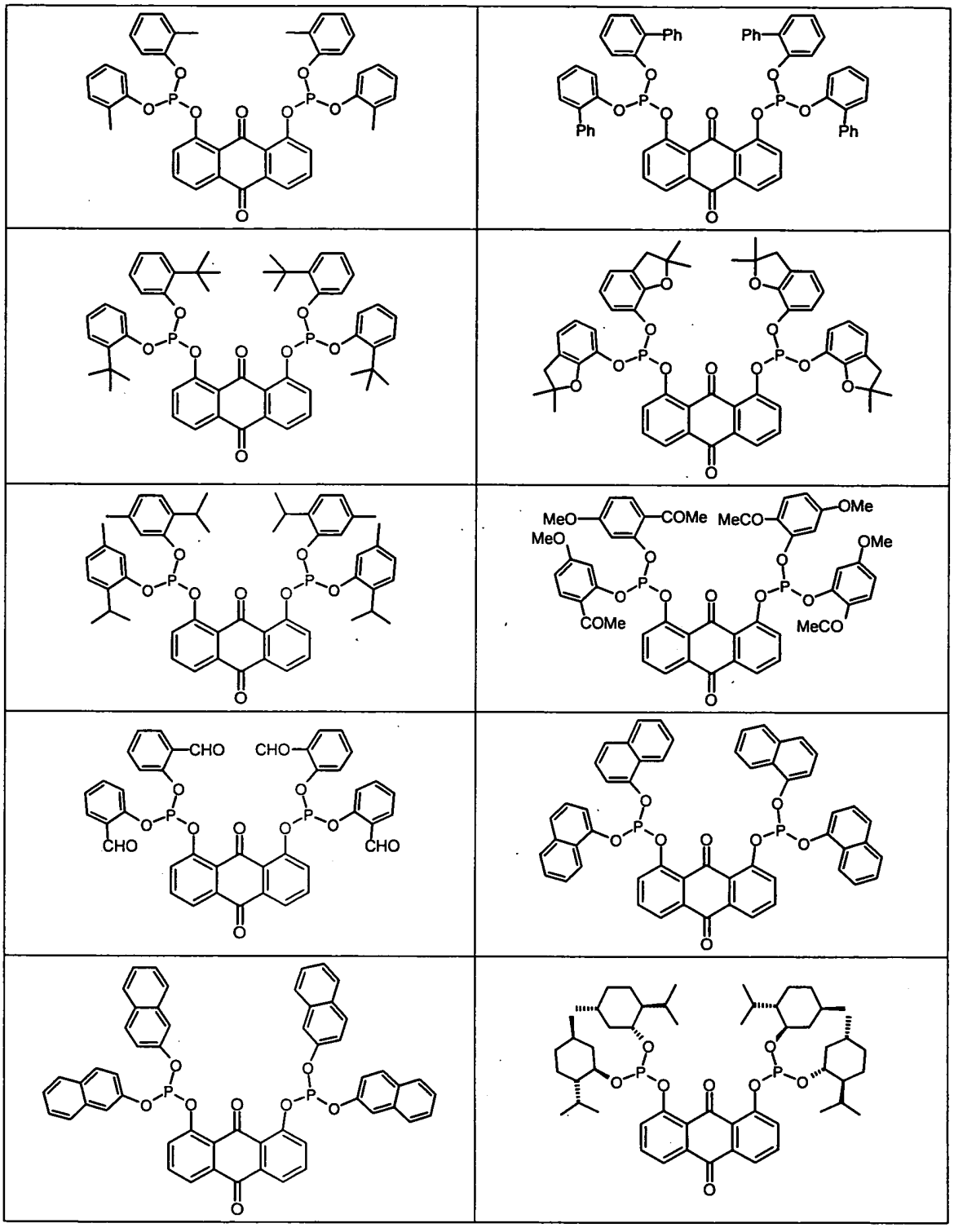
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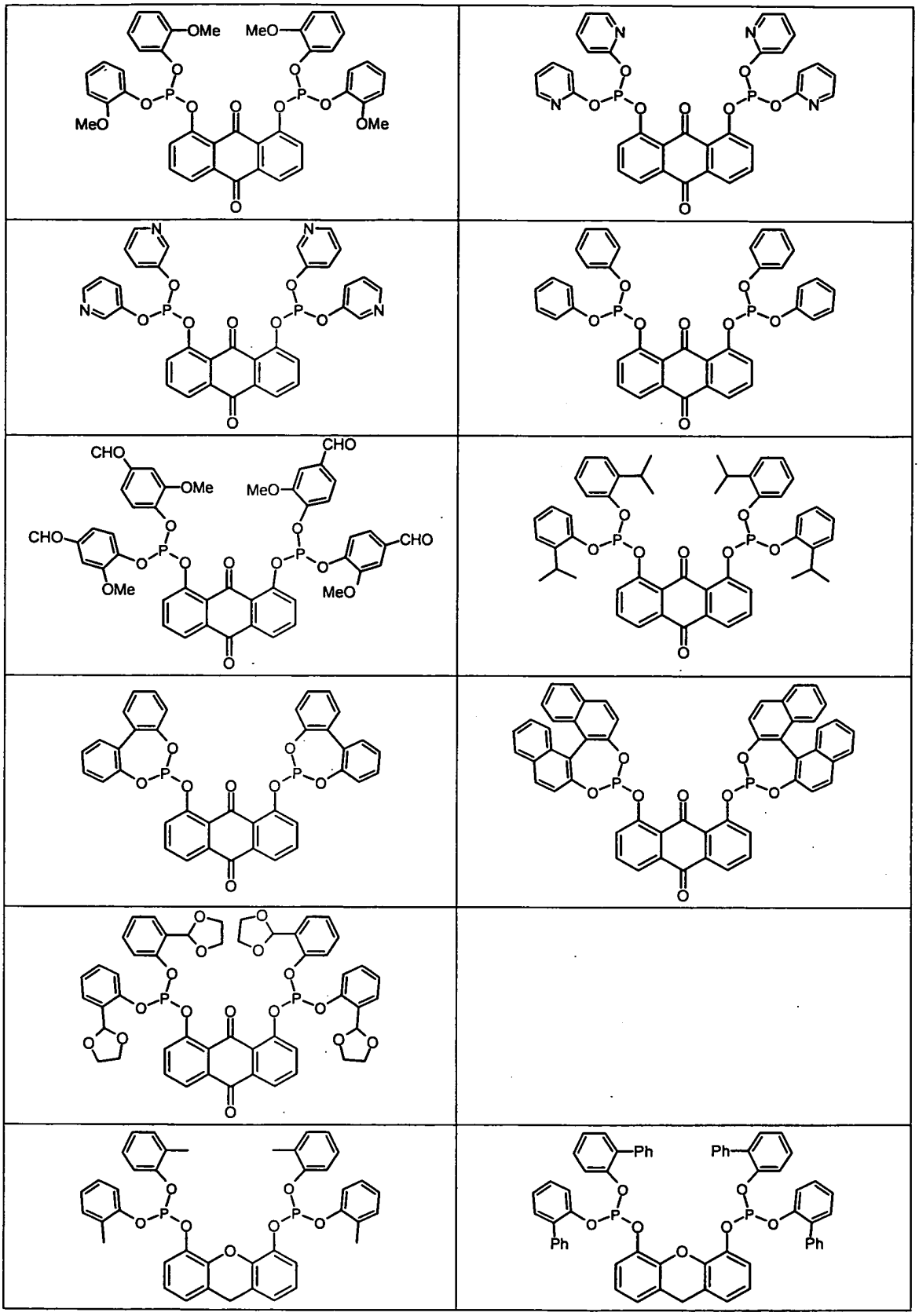

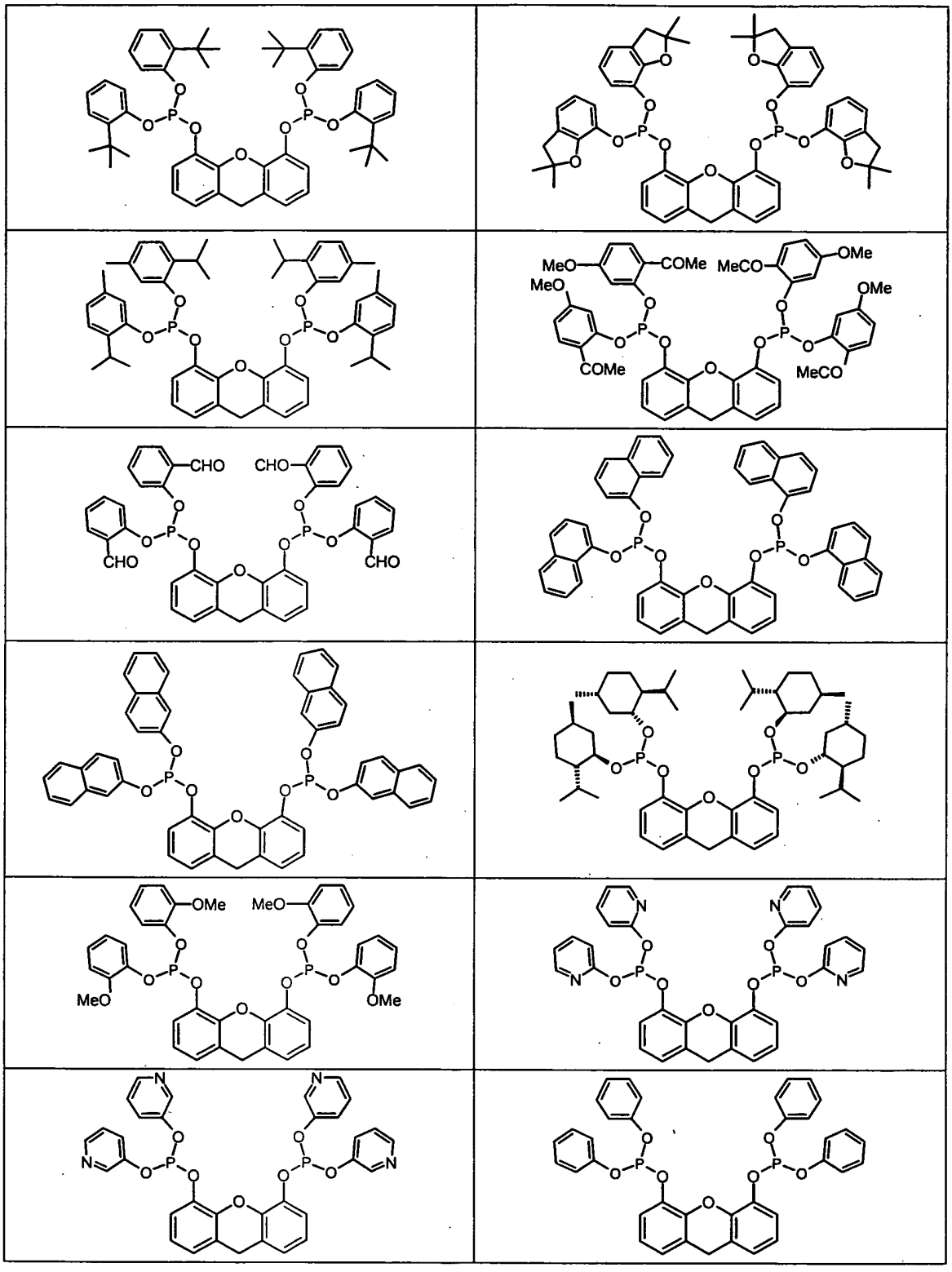
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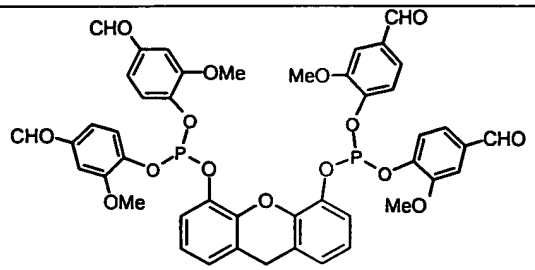
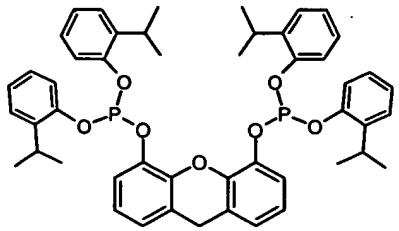
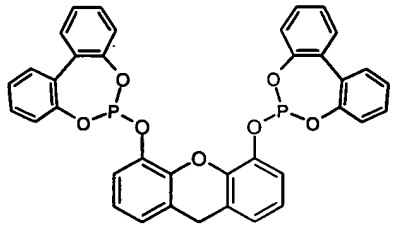
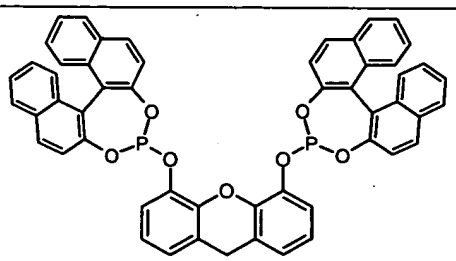
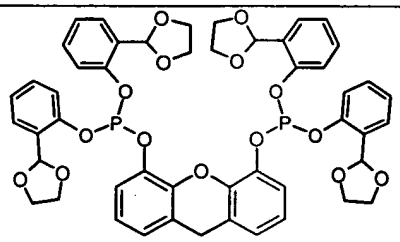
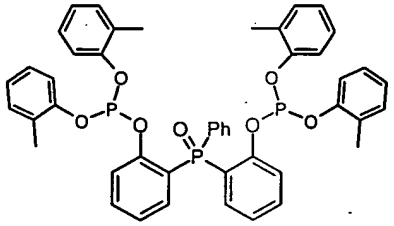
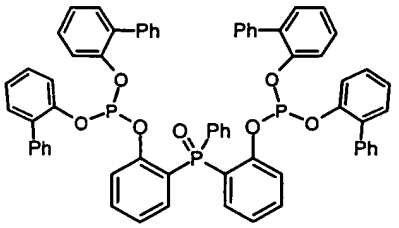
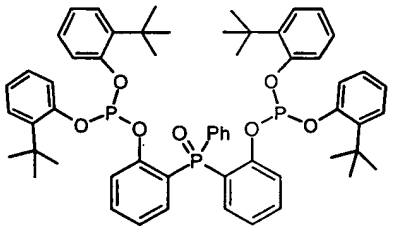
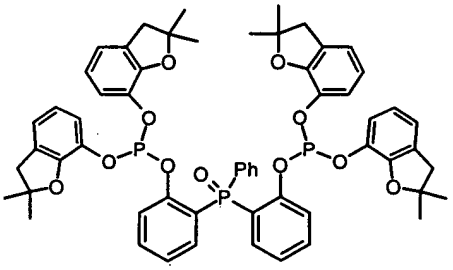
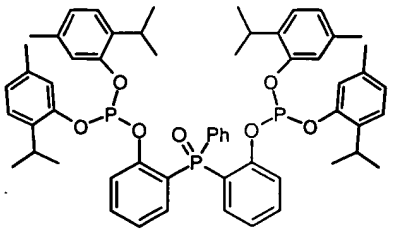
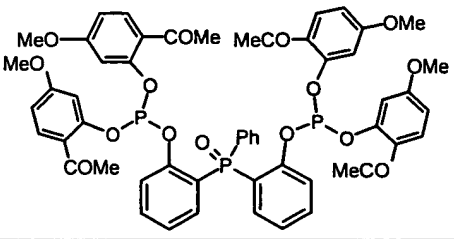
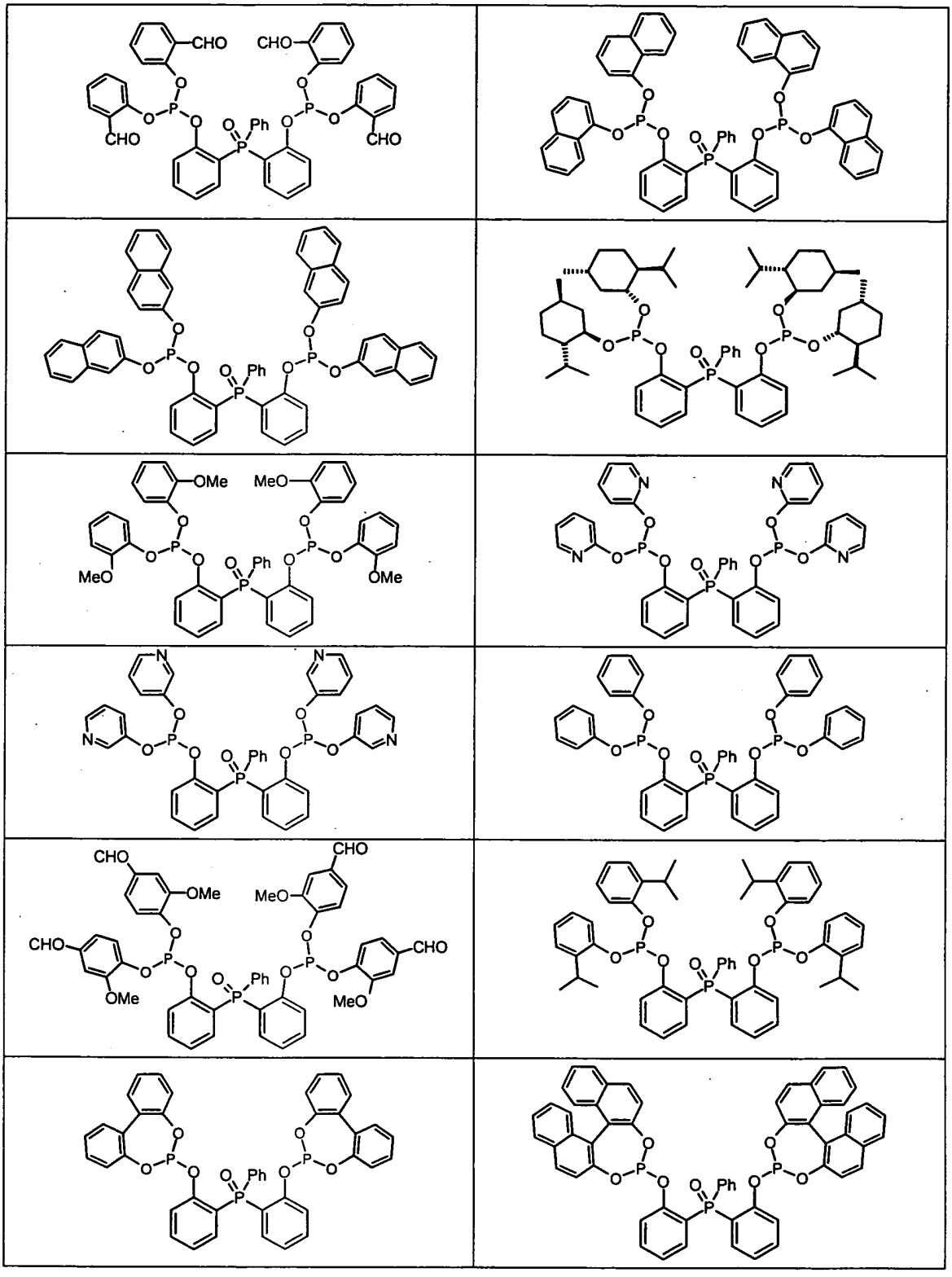
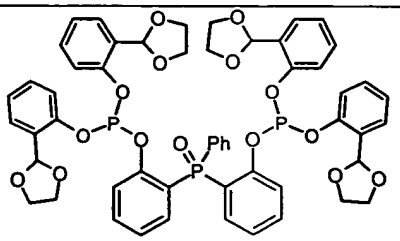
	
	
	
	
	
	



4. Process according to one of Claims 1 to 3, characterized in that the metallic element is selected from the group consisting of nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury.

5. Process according to one of the preceding claims, characterized in that the reaction is carried out in a single-phase medium.

6. Process according to one of the preceding claims, characterized in that the catalyst corresponds to the general formula (II):

$$M\ [L_f]_t \qquad (II)$$

in which
M is a transition metal,
L_f represents the organic ligand of formula (I) and
t represents a number between 1 and 4 (inclusive).

7. Process according to one of the preceding claims, characterized in that the reaction mixture comprises a solvent for the catalyst which is miscible with the phase comprising the compound to be hydrocyanated at the hydrocyanation temperature.

8. Process according to one of the preceding claims, characterized in that the transition metal compounds are nickel compounds selected from the group consisting of:

- compounds in which nickel is in oxidation state

zero, such as potassium tetracyanonickelate $K_4[Ni(CN)_4]$, bis(acrylonitrile)nickel zero, bis-(cycloocta-1,5-diene)nickel zero and derivatives containing ligands, such as tetrakis(triphenylphosphine)nickel zero;

- compounds of nickel such as carboxylates, carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite, phosphate and derivatives, iodide, nitrate, sulphate, sulphite, aryl- and alkylsulphonates.

9. Process according to one of the preceding claims, characterized in that the organic compounds containing at least one ethylenic double bond are selected from diolefins such as butadiene, isoprene, hexa-1,5-diene, cycloocta-1,5-diene, ethylenically unsaturated aliphatic nitriles, especially linear pentenenitriles such as pent-3-enenitrile and pent-4-enenitrile, monoolefins such as styrene, methylstyrene, vinylnaphthalene, cyclohexene and methylcyclohexene and also mixtures of two or more of these compounds.

10. Process according to one of the preceding claims, characterized in that the amount of compound of nickel or of another transition metal used is selected such that per mole of organic compound to be hydrocyanated or isomerized between 10^{-4} and 1 mol of nickel or of the other transition metal is employed and in that the amount of organic ligand of formula (I) used is selected such that the number of moles of this compound relative to 1 mol of transition metal is from 0.5 to 50.

11. Process according to one of the preceding claims, characterized in that the hydrocyanation reaction is carried out at a temperature from 10°C to 200°C.

12. Process according to one of the preceding claims for hydrocyanating ethylenically unsaturated nitrile compounds to dinitriles by reaction with hydrogen cycanide, characterized in that it is operated in the presence of a catalyst system comprising at least one transition metal compound, at least one organic compound of formula (I) and a cocatalyst composed of at least one Lewis acid.

13. Process according to Claim 12, characterized in that the ethylenically unsaturated nitrile compounds are selected from ethylenically unsaturated aliphatic nitriles comprising linear pentenenitriles such as pent-3-enenitrile and pent-4-enenitrile and mixtures thereof.

14. Process according to Claim 13, characterized in that the linear pentenenitriles contain amounts of other compounds selected from the group consisting of 2-methylbut-3-enenitrile, 2-methylbut-2-enenitrile, pent-2-enenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile and butadiene.

15. Process according to one of Claims 12 to 14, characterized in that the Lewis acid employed as cocatalyst is selected from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements.

16. Process according to one of Claims 12 to 15, characterized in that the Lewis acid is selected from salts selected from the group of halides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkylsulphonates, haloalkylacetates, perhaloalkylacetates, carboxylates and phosphates.

17. Process according to one of Claims 12 to 16,

characterized in that the Lewis acid is selected from zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, indium trifluoroacetate, zinc trifluoroacetate, the chlorides or bromides of rare earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, and cobalt chloride, ferrous chloride, yttrium chloride and mixtures thereof.

18. Process according to one of Claims 12 to 17, characterized in that the Lewis acid employed represents from 0.01 to 50 mol per mole of transition metal compound.

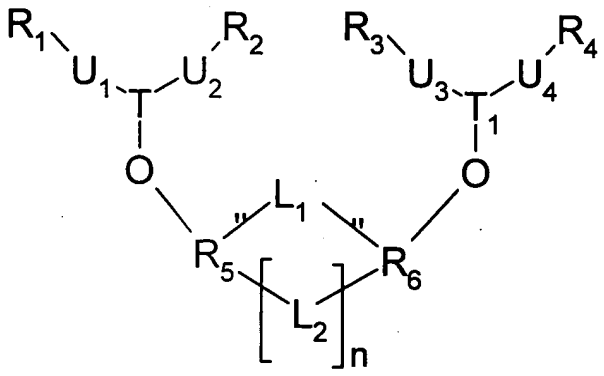
19. Process according to one of Claims 1 to 18, characterized in that 2-methylbut-3-enenitrile, present in the reaction mixture originating from butadiene hydrocyanation, is isomerized to pentenenitriles in the absence of hydrogen cyanide, in the presence of a catalyst comprising at least one organic ligand of general formula (I) and at least one transition metal compound.

20. Process according to Claim 19, characterized in that the 2-methylbut-3-enenitrile subjected to isomerization is employed alone or in a mixture with 2-methylbut-2-enenitrile, pent-4-enenitrile, pent-3-enenitrile, pent-2-enenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

21. Process according to either of Claims 19 and 20, characterized in that the isomerization reaction is carried out at a temperature from 10°C to 200°C.

22. Process according to Claims 19 to 21, characterized in that the isomerization of 2-methylbut-3-enenitrile to pentenenitriles is carried out in the presence of at least one transition metal compound, at least one organic phosphorous ligand of the formula (I) and a cocatalyst composed of at least one Lewis acid.

23. Organophosphorus compounds corresponding to the general formula I below:



(I)

in which:

T and T_1, which are identical or different, represent a phosphorus, arsenic or antimony atom,

R_1, R_2, R_3 and R_4, which are identical or different, represent a substituted or unsubstituted, aromatic, aliphatic or cycloaliphatic radical comprising one or more rings, which are in fused form or not and which may contain one or more heteroatoms, where the radicals R_1 and R_2 on the one hand and R_3 and R_4 on the other hand may be interconnected by a covalent bond, a hydrocarbon chain or a heteroatom,

U_1, U_2, U_3 and U_4, which are identical or different, represent an oxygen atom or a radical of formula NR in which R denotes a monovalent alkyl, aryl, cycloalkyl, sulphonyl or carbonyl radical,

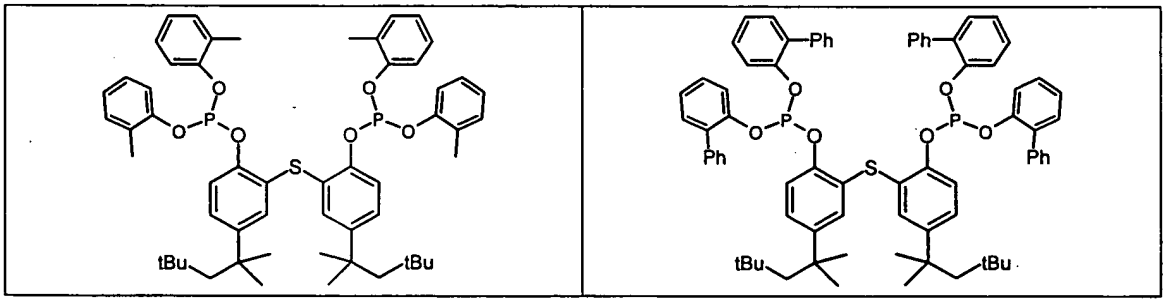
R_5 and R_6, which are identical or different, represent an aryl or cycloaliphatic group which may comprise heteroatoms and/or one or more rings, in fused form or not, and which are substituted or unsubstituted,

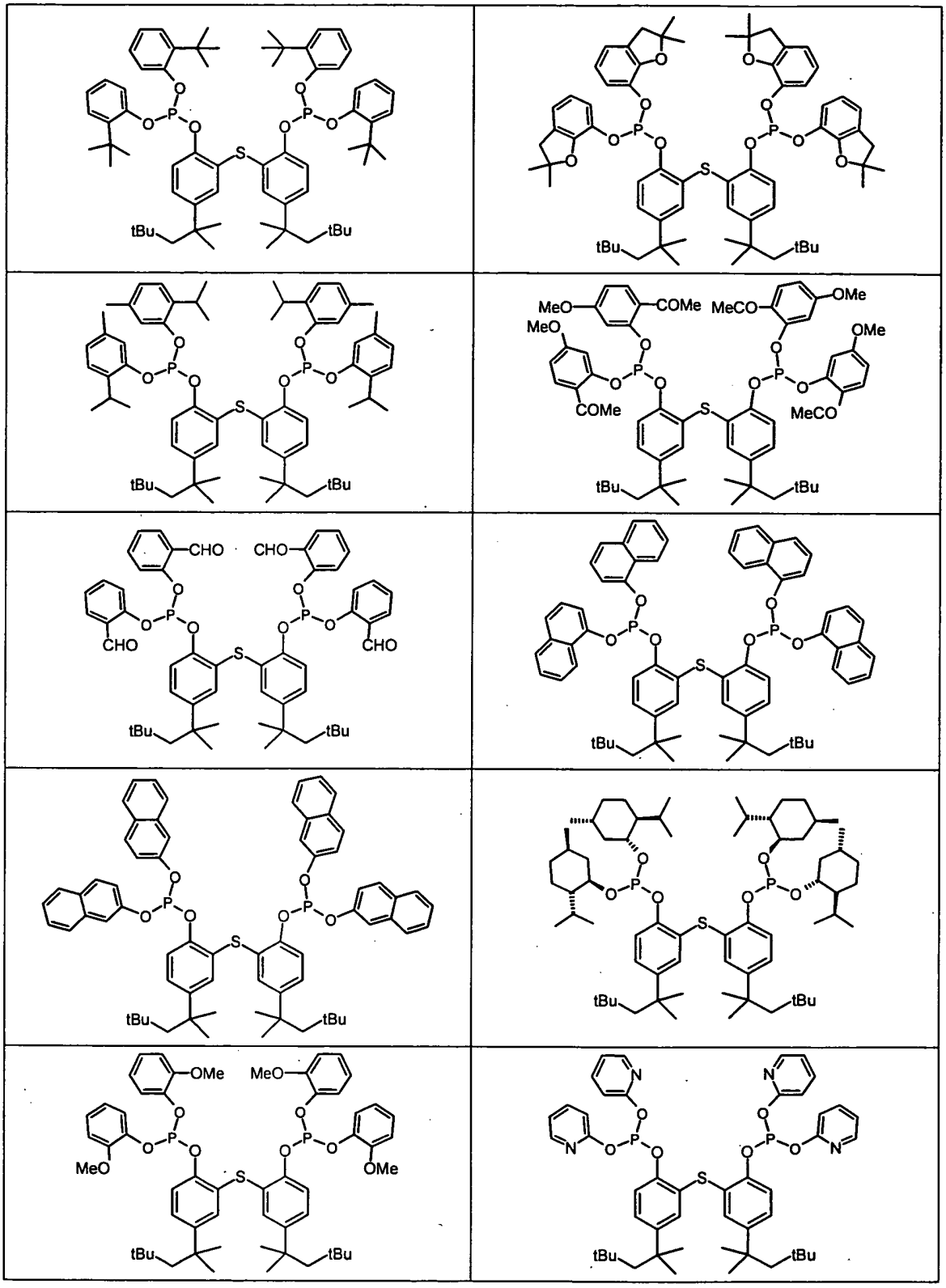
n is an integer equal to 0 or 1,

L_1, when n is 0, represents a divalent radical selected from the group consisting of the groups NR_7, PR_8, SiR_9R_{10}, BR_{11}, S, POR_{12}, SO_2 and CO, in which R_7 is as defined for R above, R_8 and R_{12} may represent the radical OR_{13}, and R_8, R_9, R_{10}, R_{11}, R_{12} and R_{13} represent alkyl, aryl or cycloalkyl radicals,

L_1 and L_2, when n is 1, are identical or different and represent a covalent bond or a radical selected from the group consisting of the groups O, NR_7, PR_8, SiR_9R_{10}, BR_{11}, S, POR_{12}, SO_2, CO and $-CR_{14}R_{15}-$, in which R_7 is as defined for R above, R_8 and R_{12} may represent the radical OR_{13}, and R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} represent alkyl, aryl or cycloalkyl radicals, it being possible also for R_{14} and R_{15} to represent a hydrogen atom.

24. Compounds according to Claim 23, corresponding to the formulae below:

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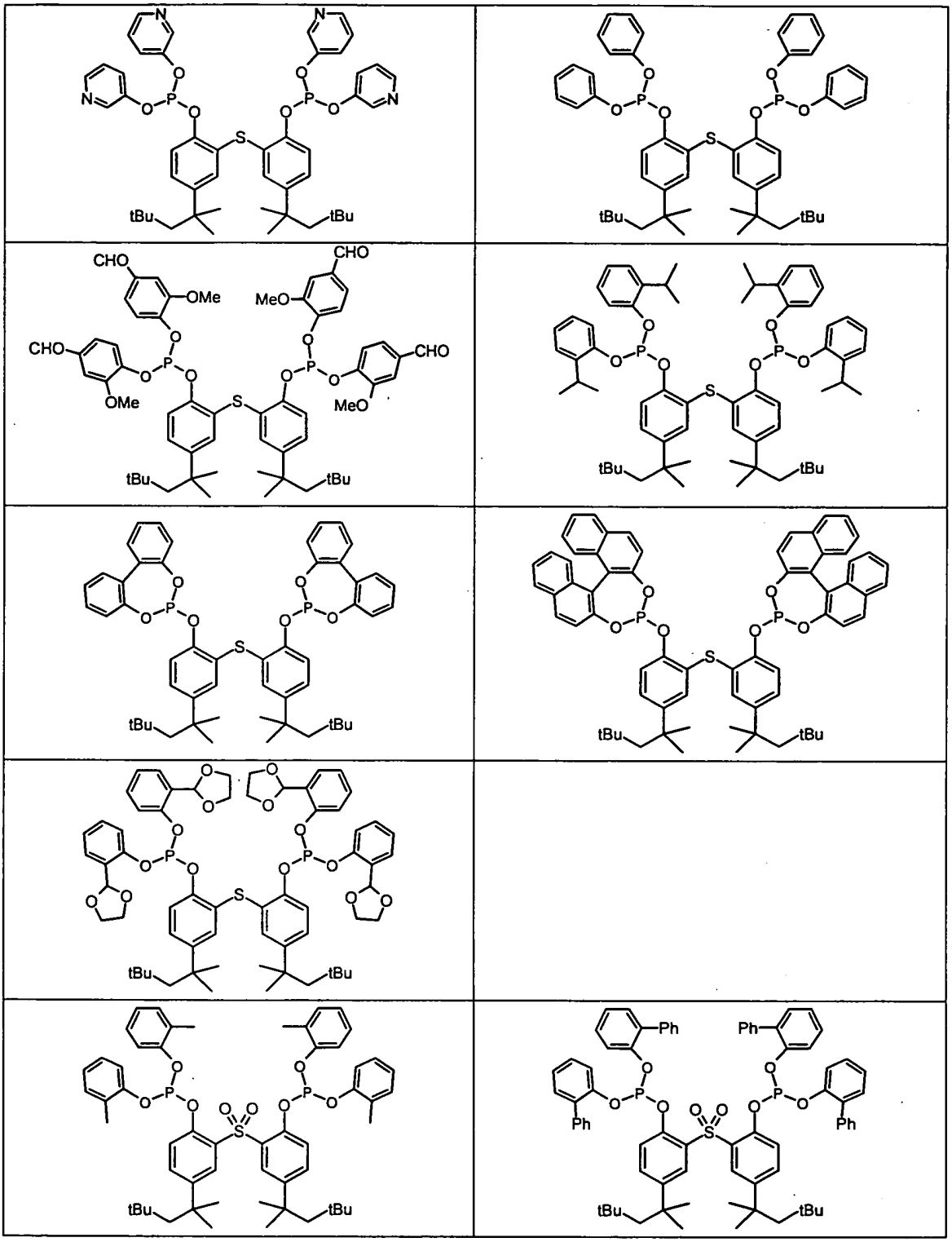

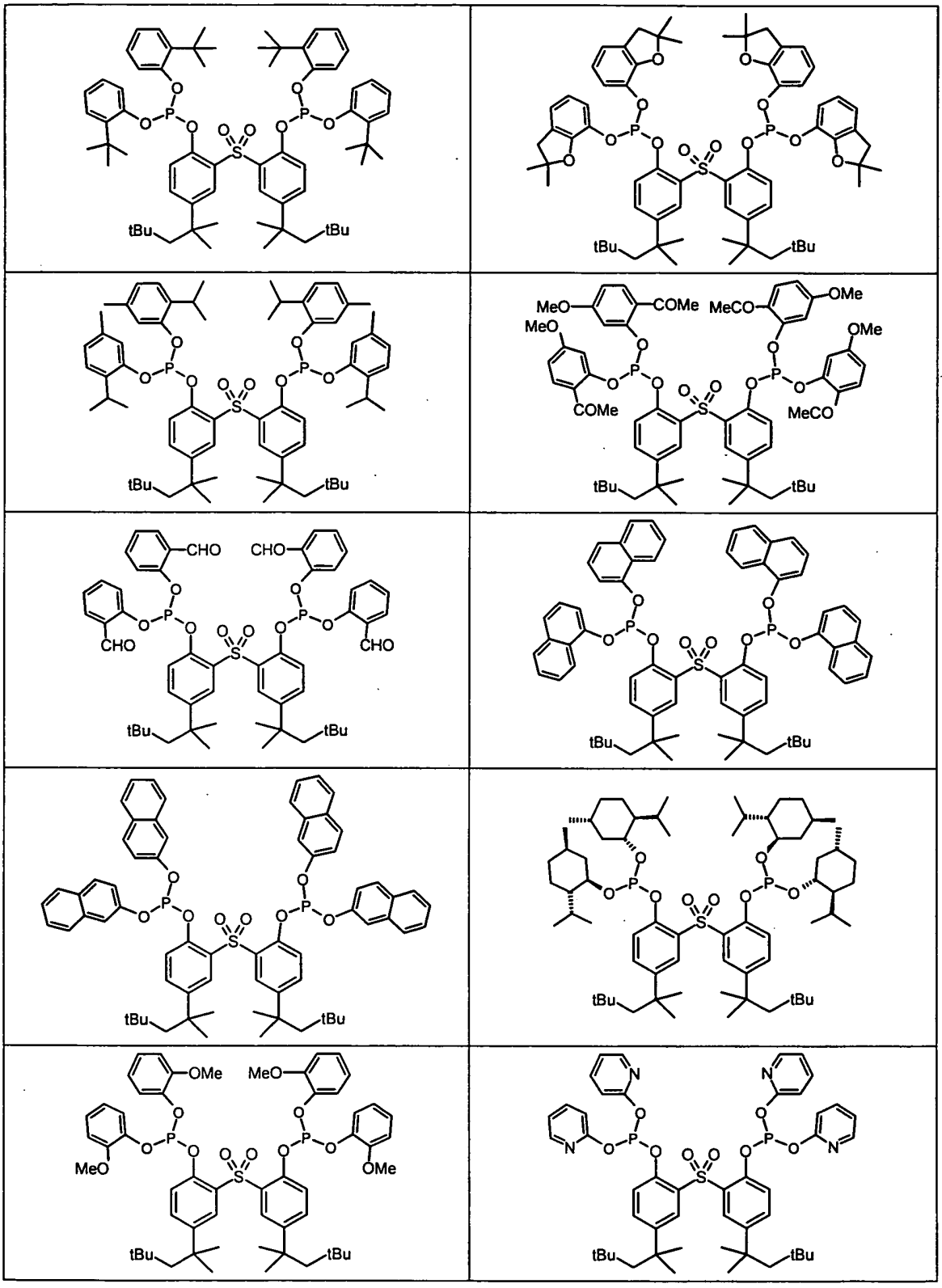
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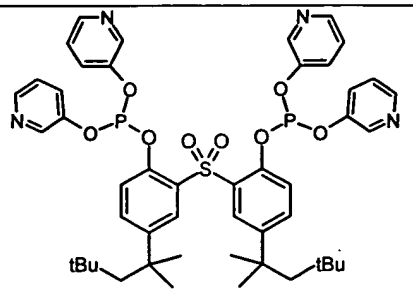	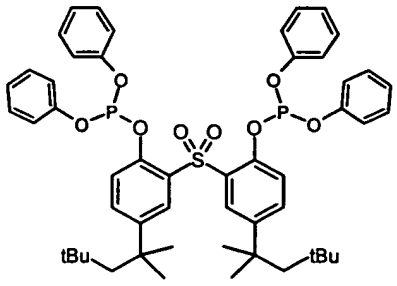
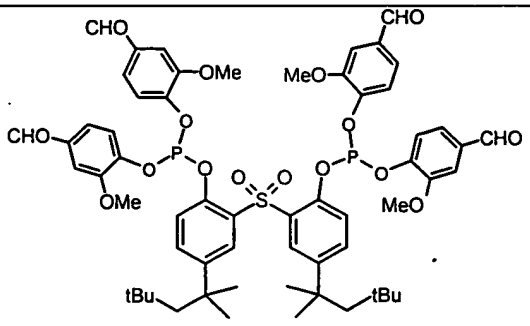	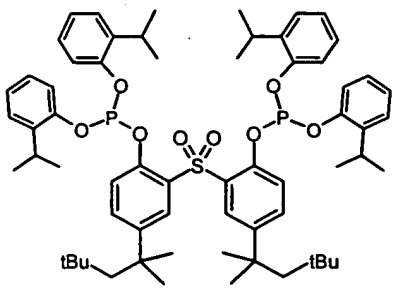
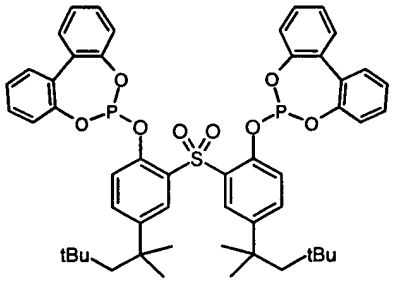	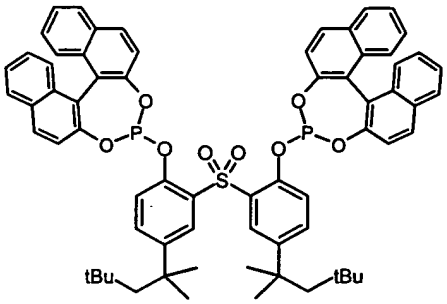
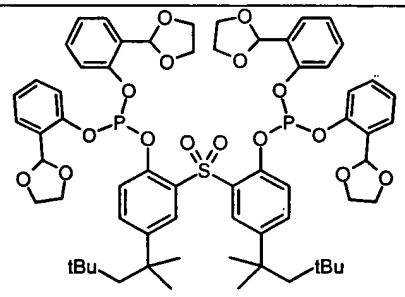	
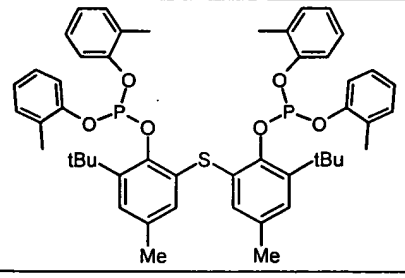	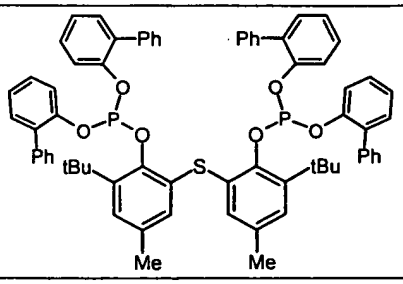

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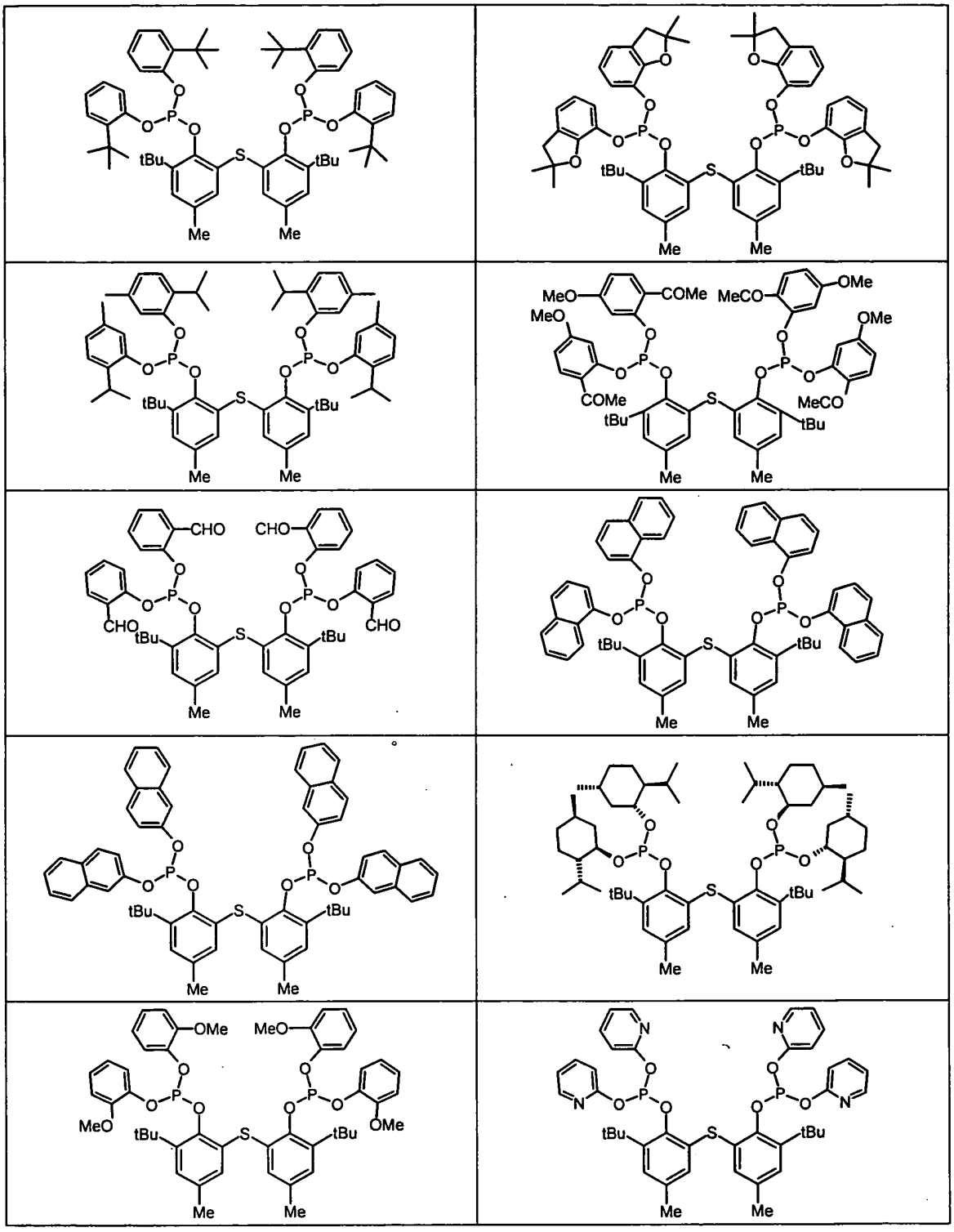

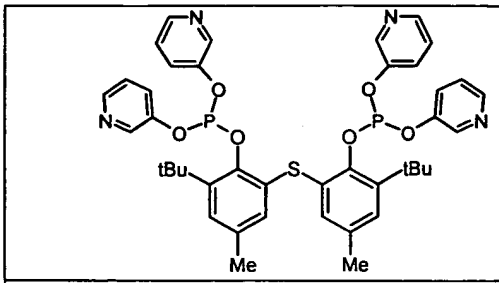
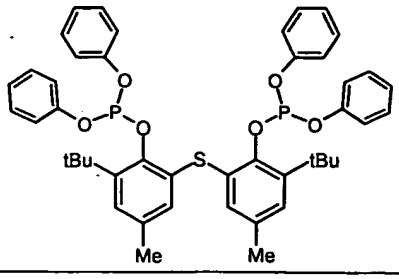
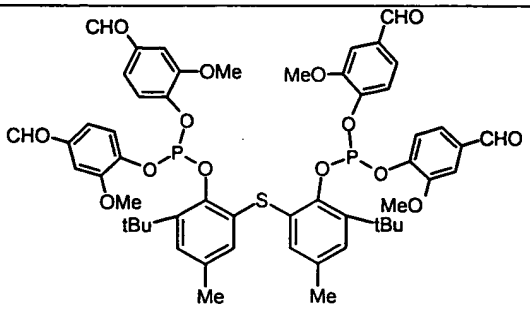
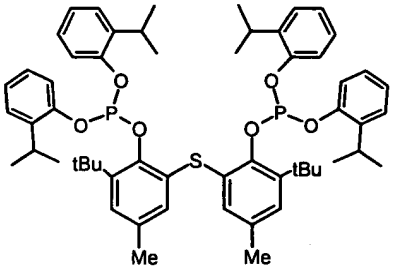
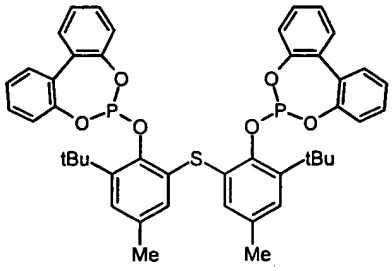
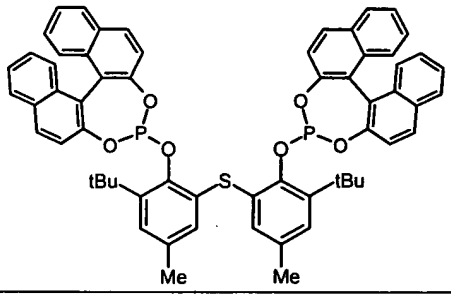
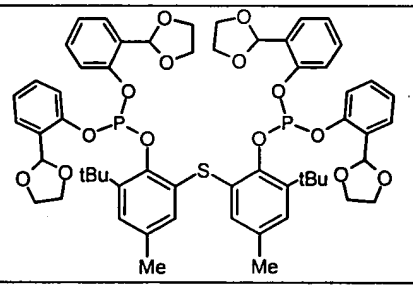

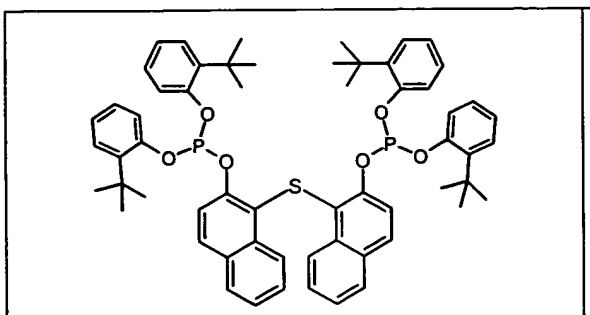

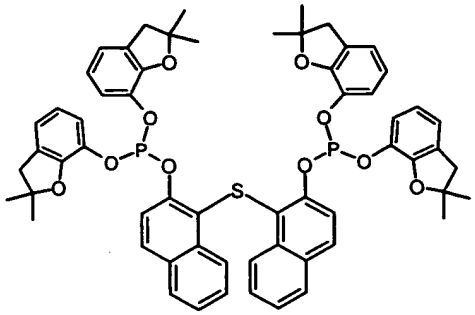

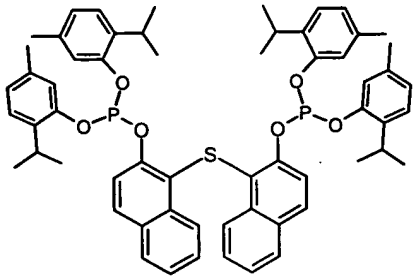

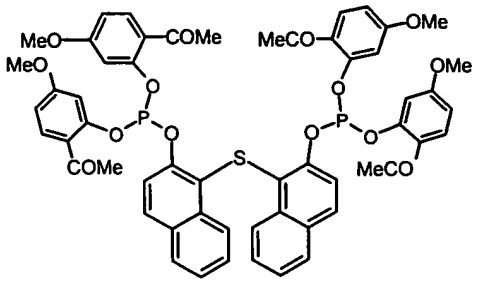
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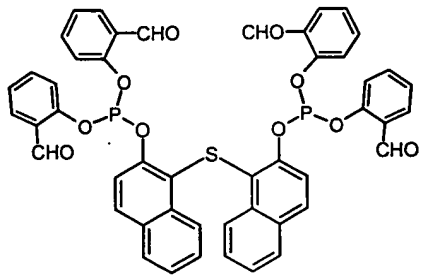
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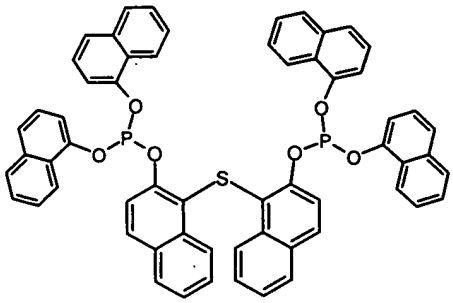

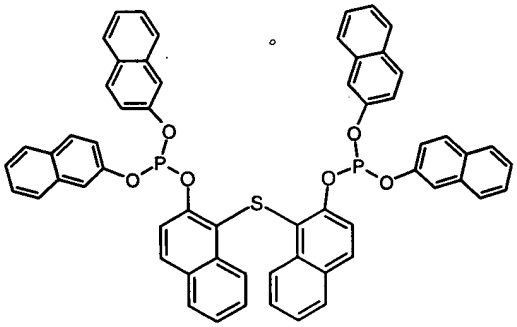

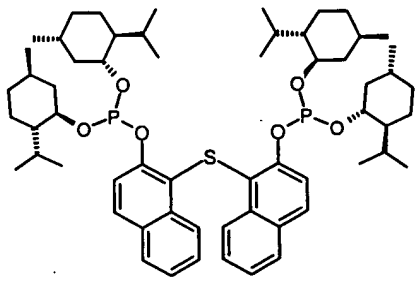

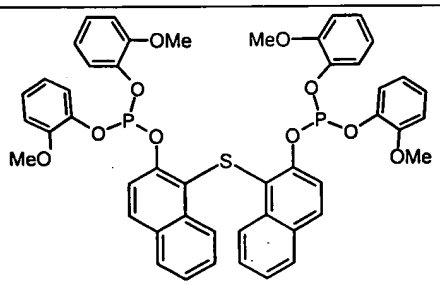
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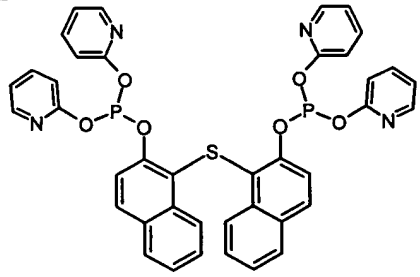
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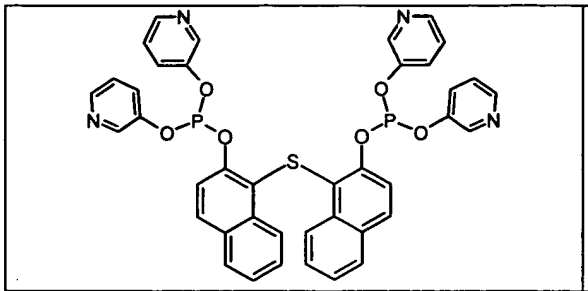

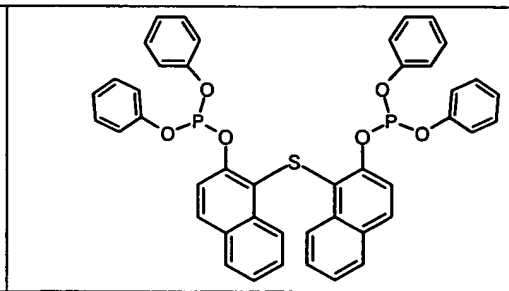

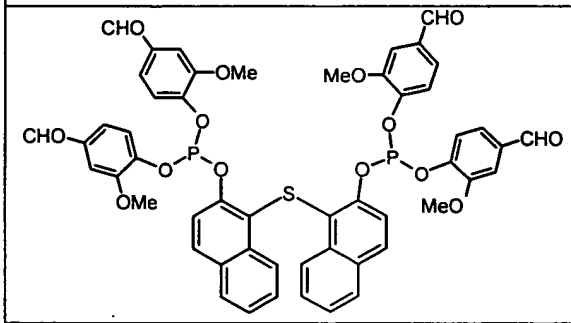

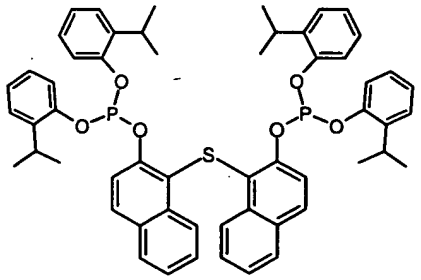

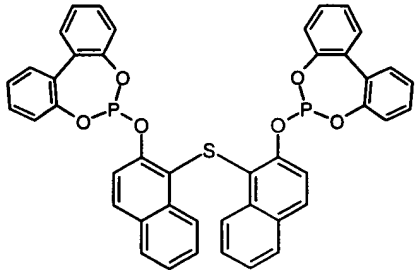

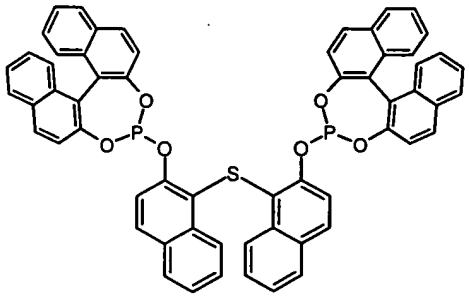

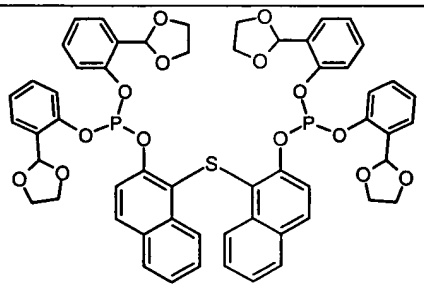

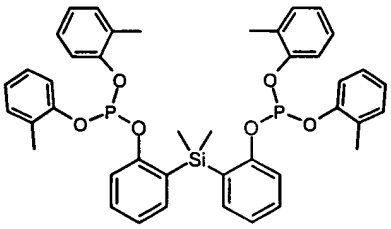

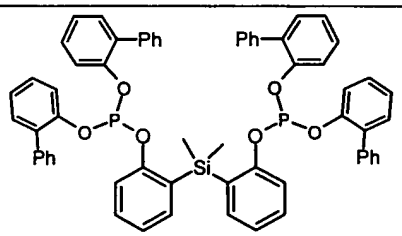

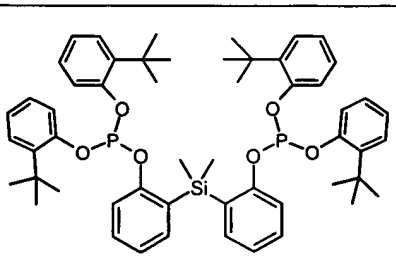

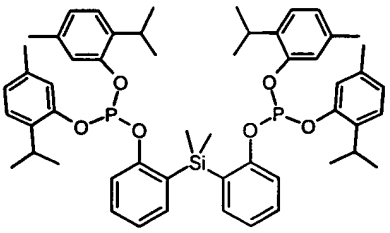	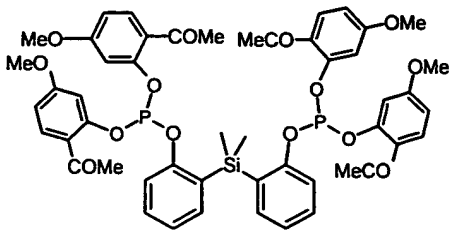
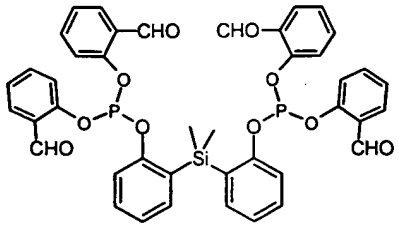	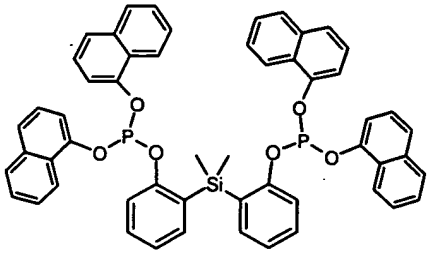
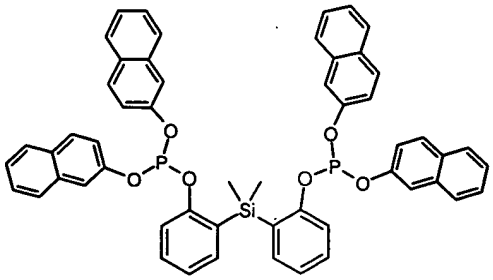	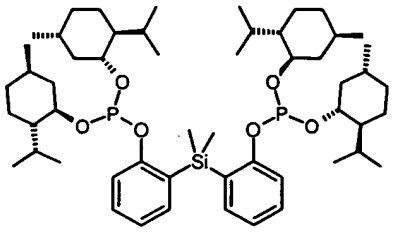
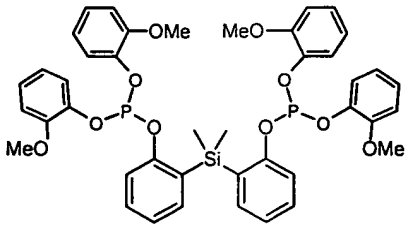	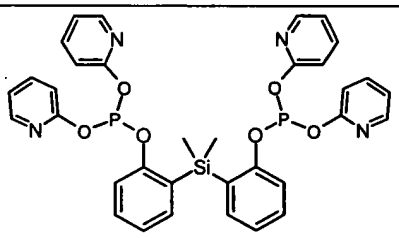
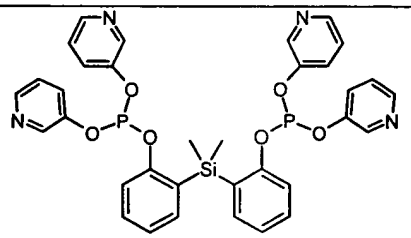	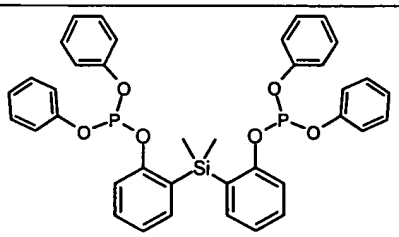
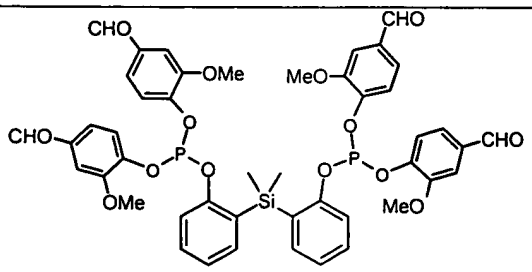	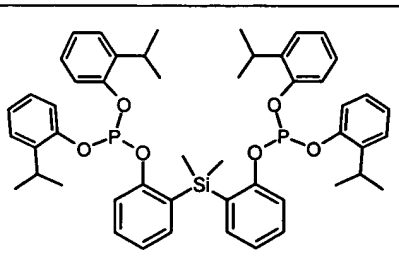

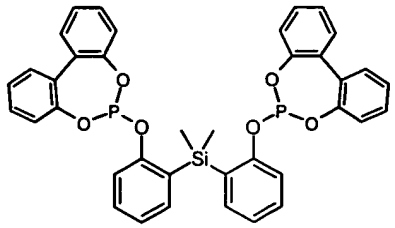	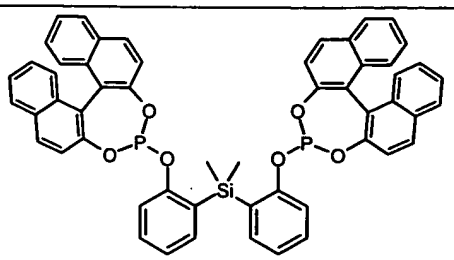
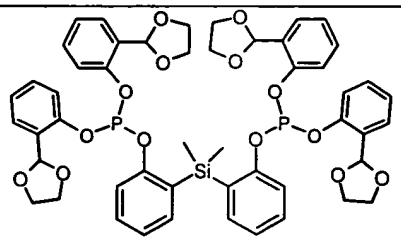	
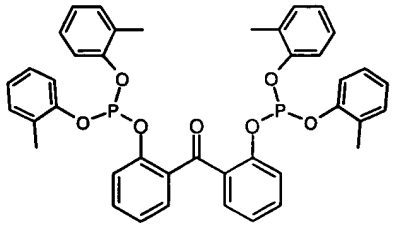	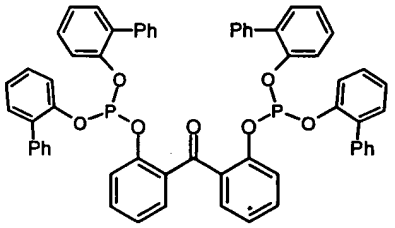
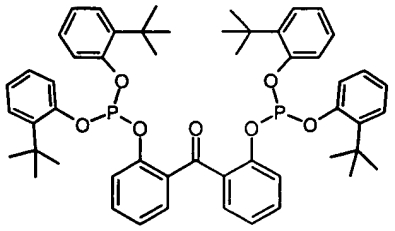	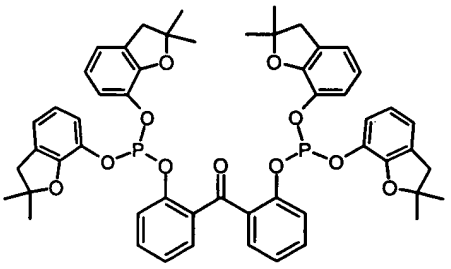
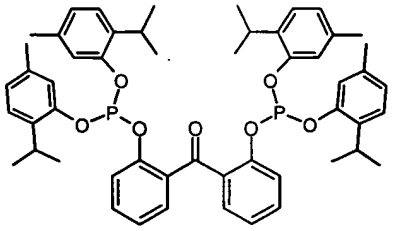	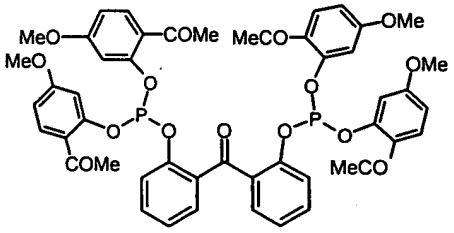
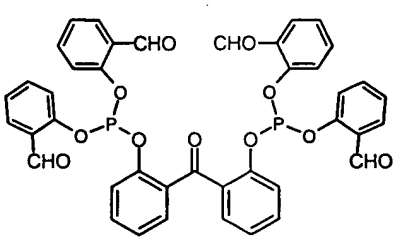	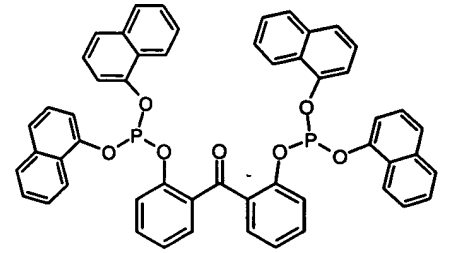

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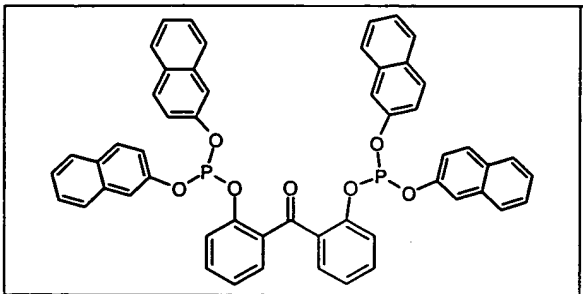

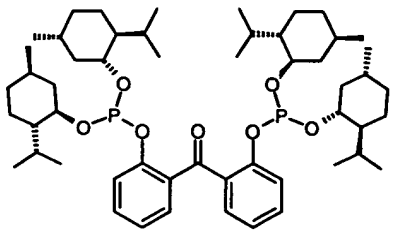

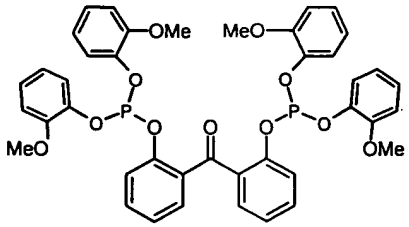
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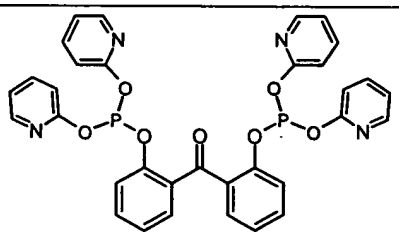
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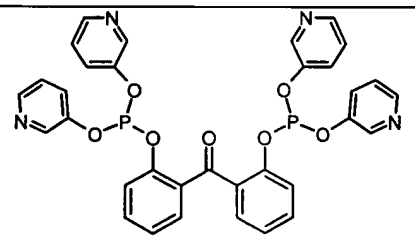
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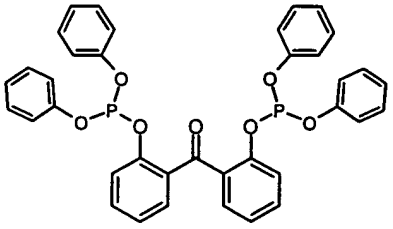

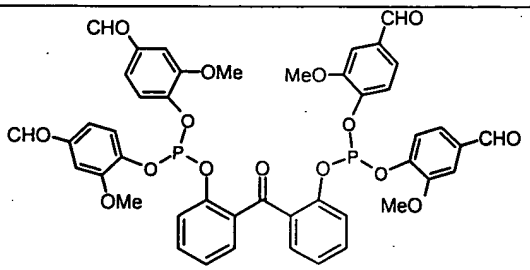
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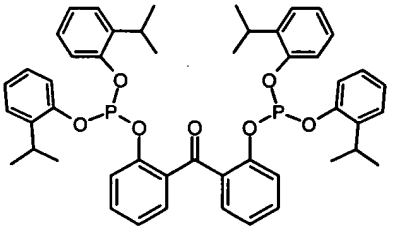

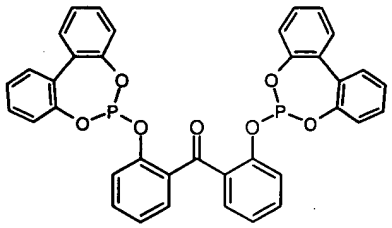

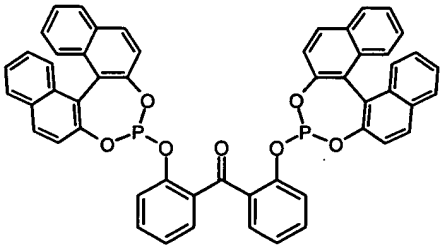

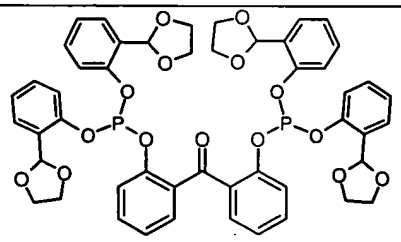

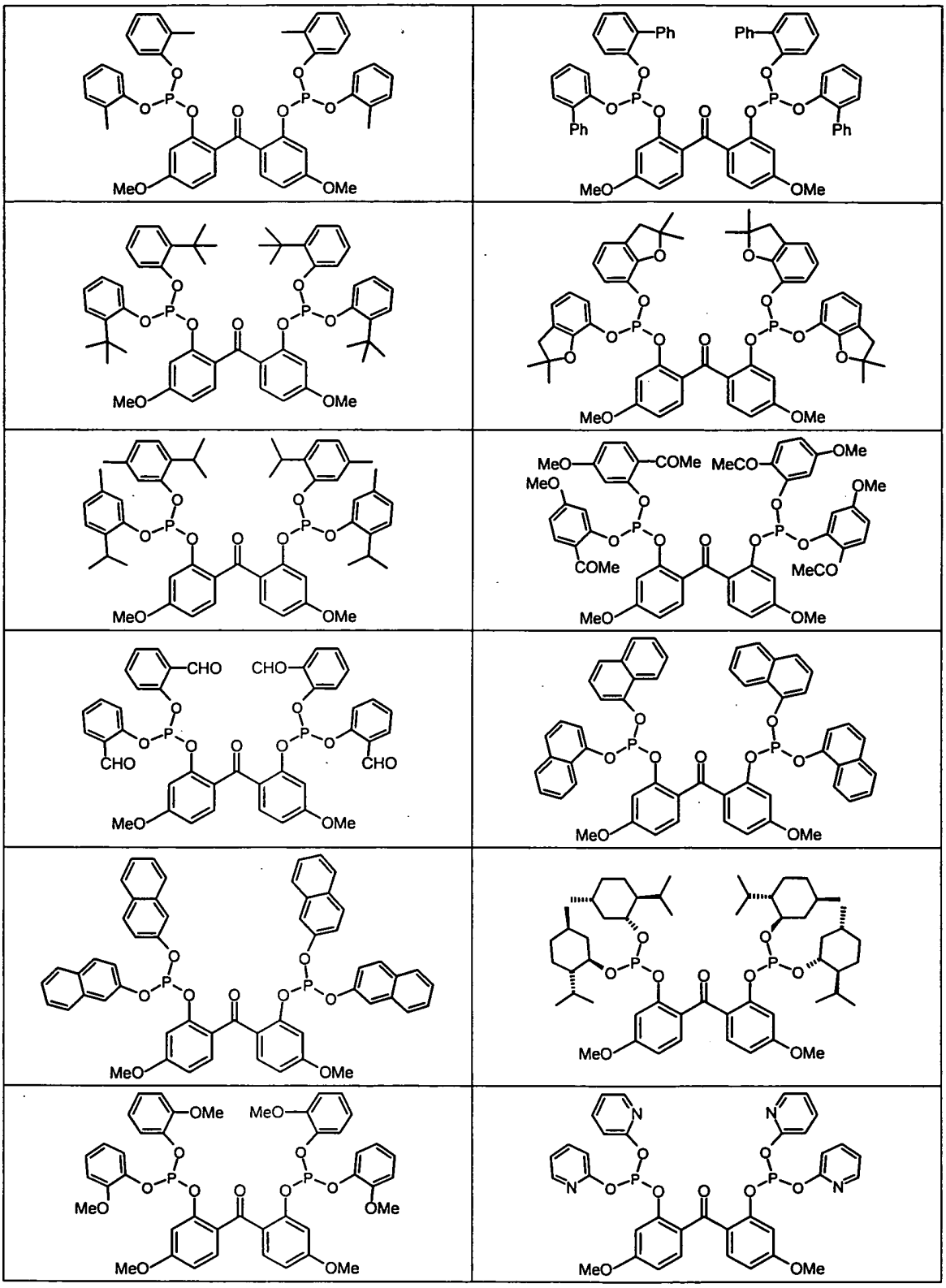
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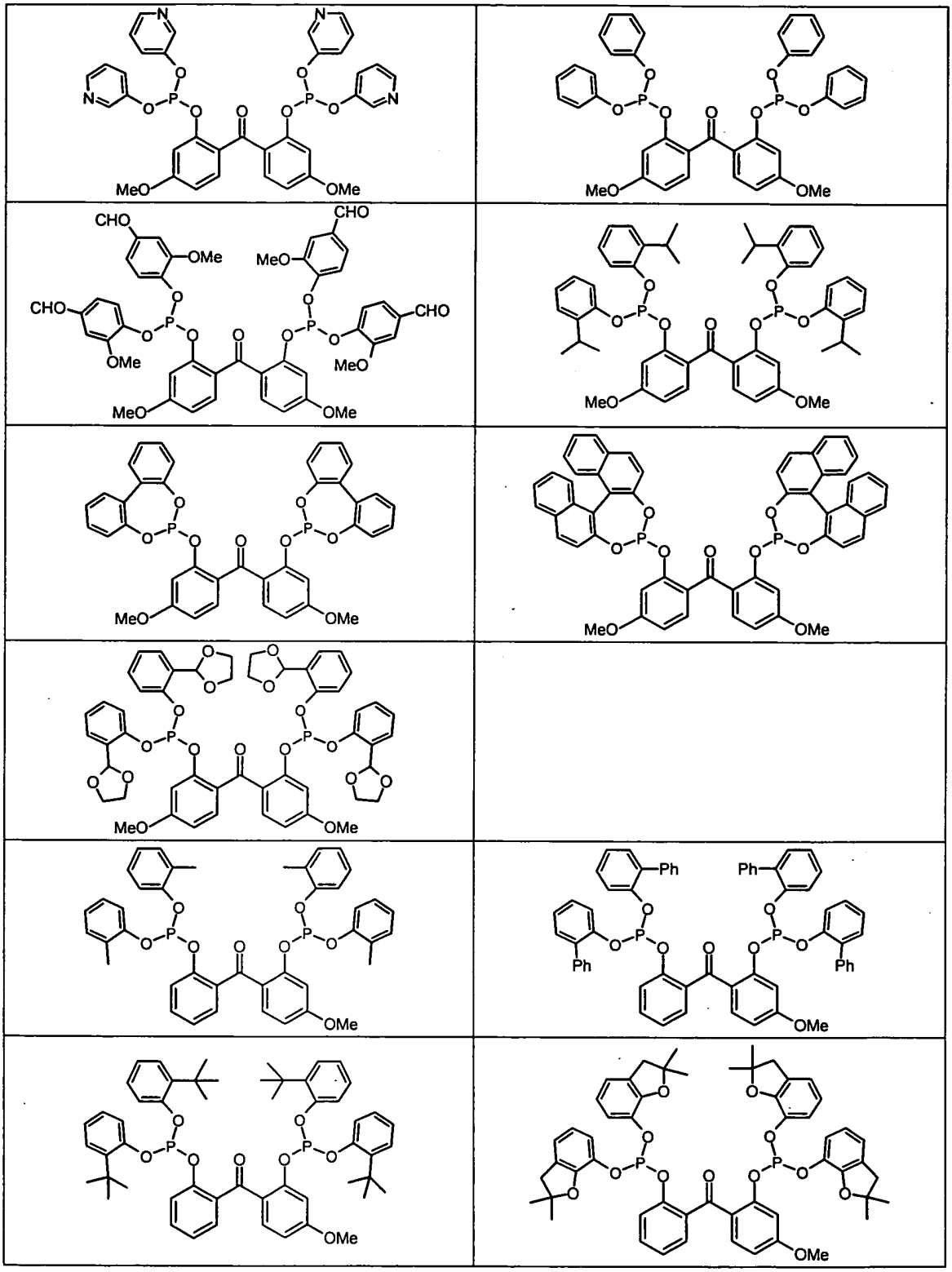

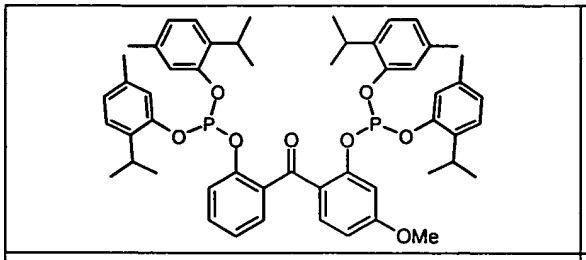
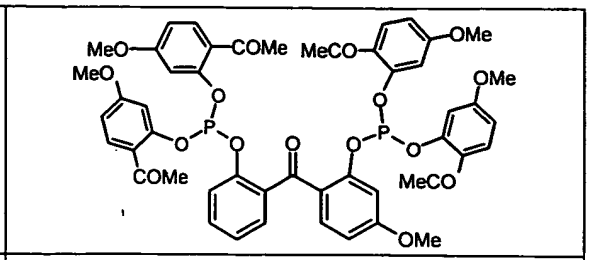
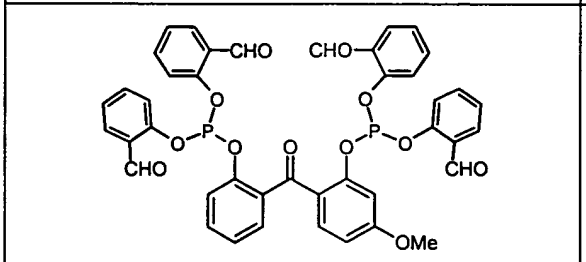
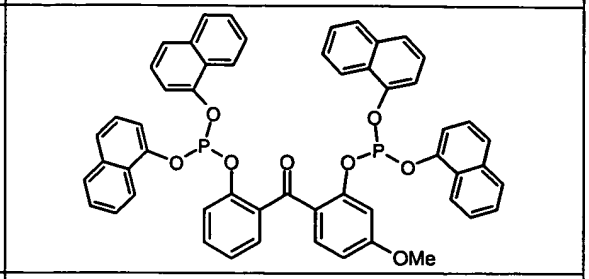
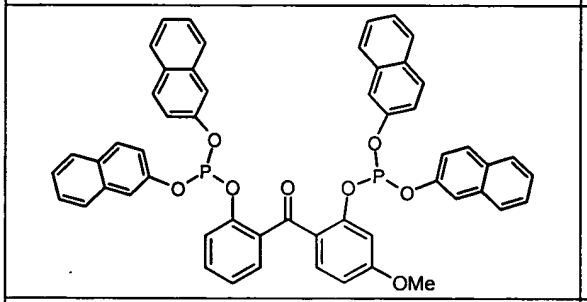
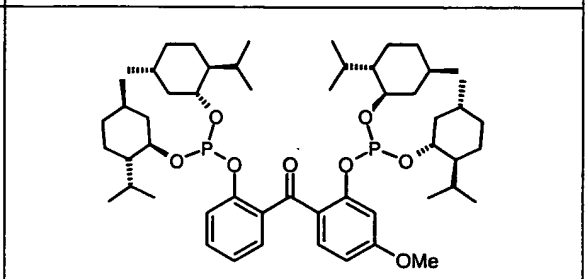
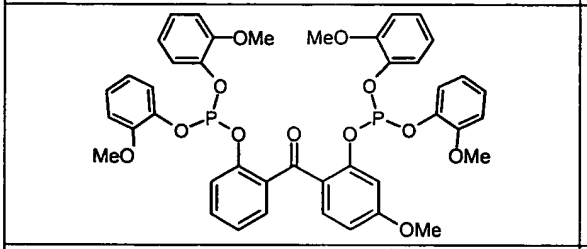
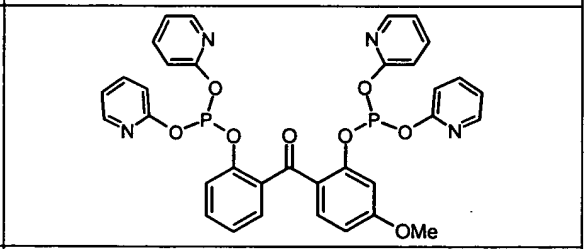
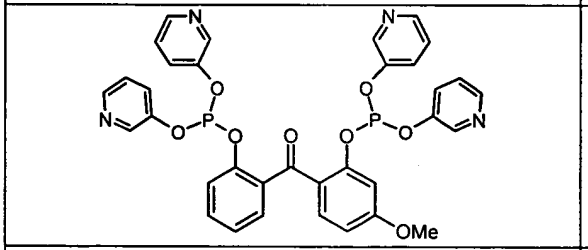
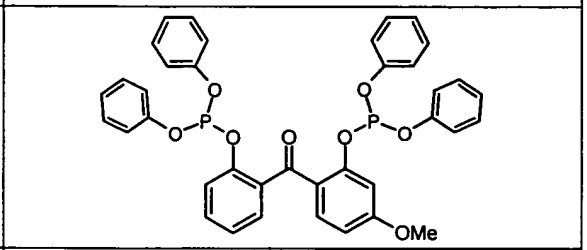
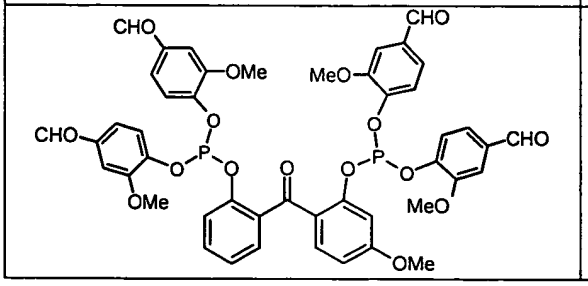
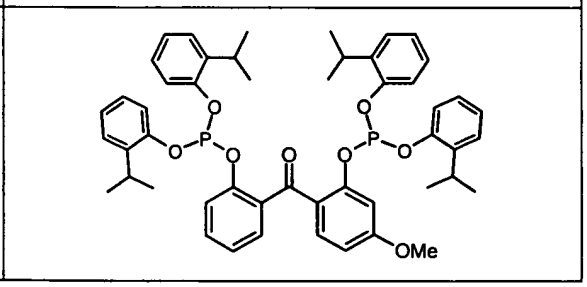

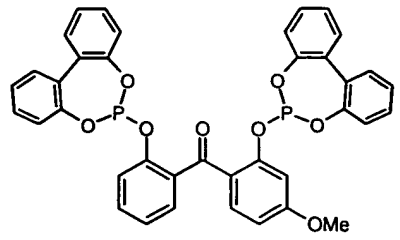	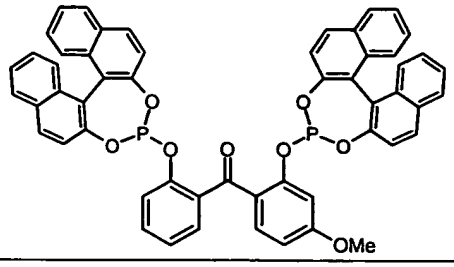
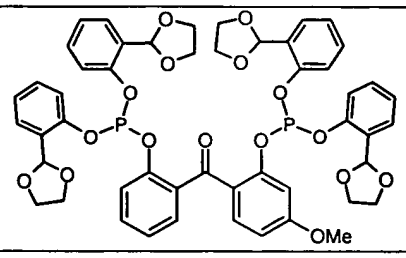	
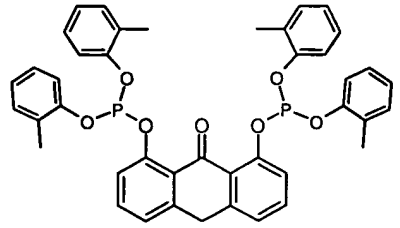	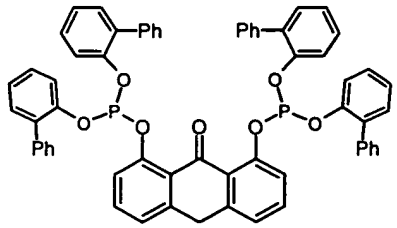
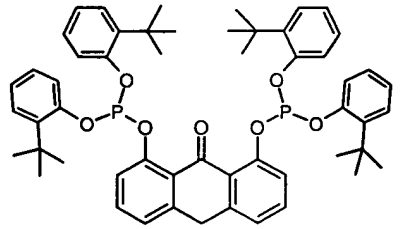	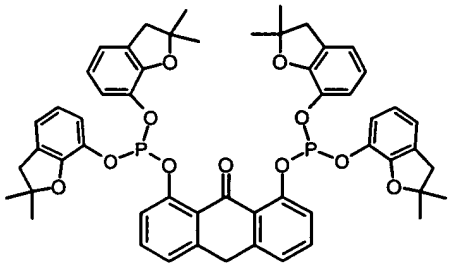
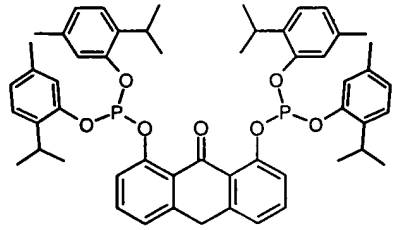	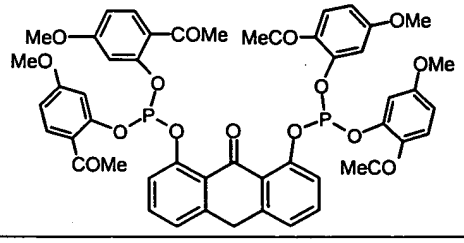
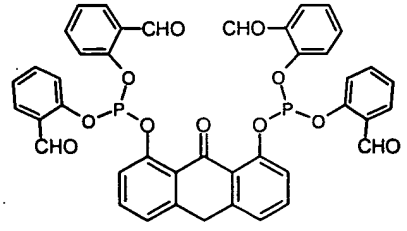	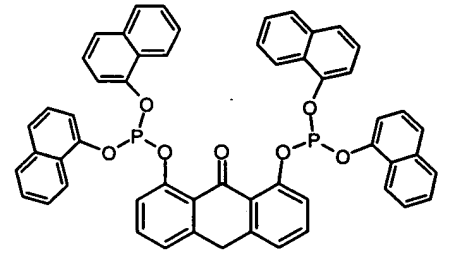

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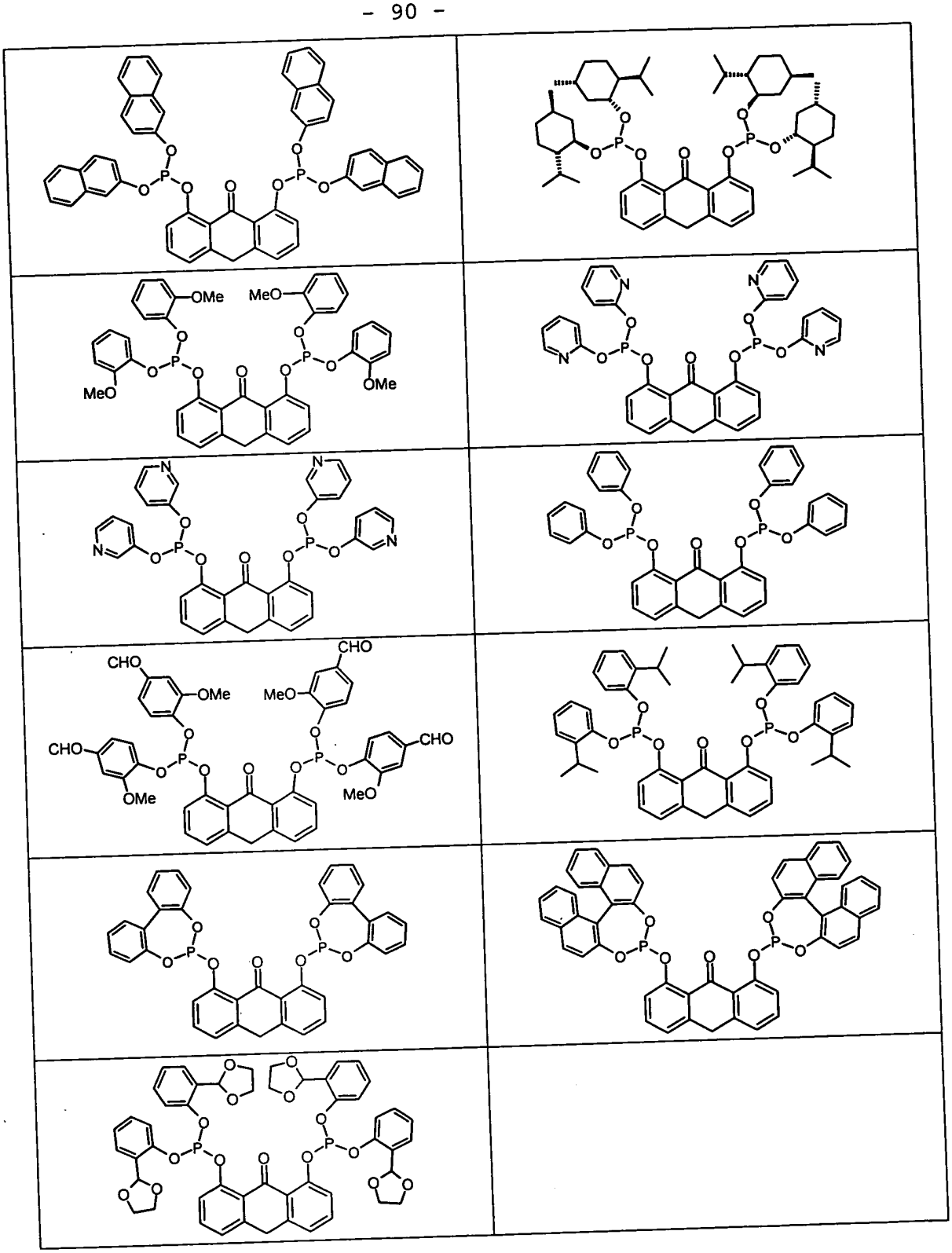
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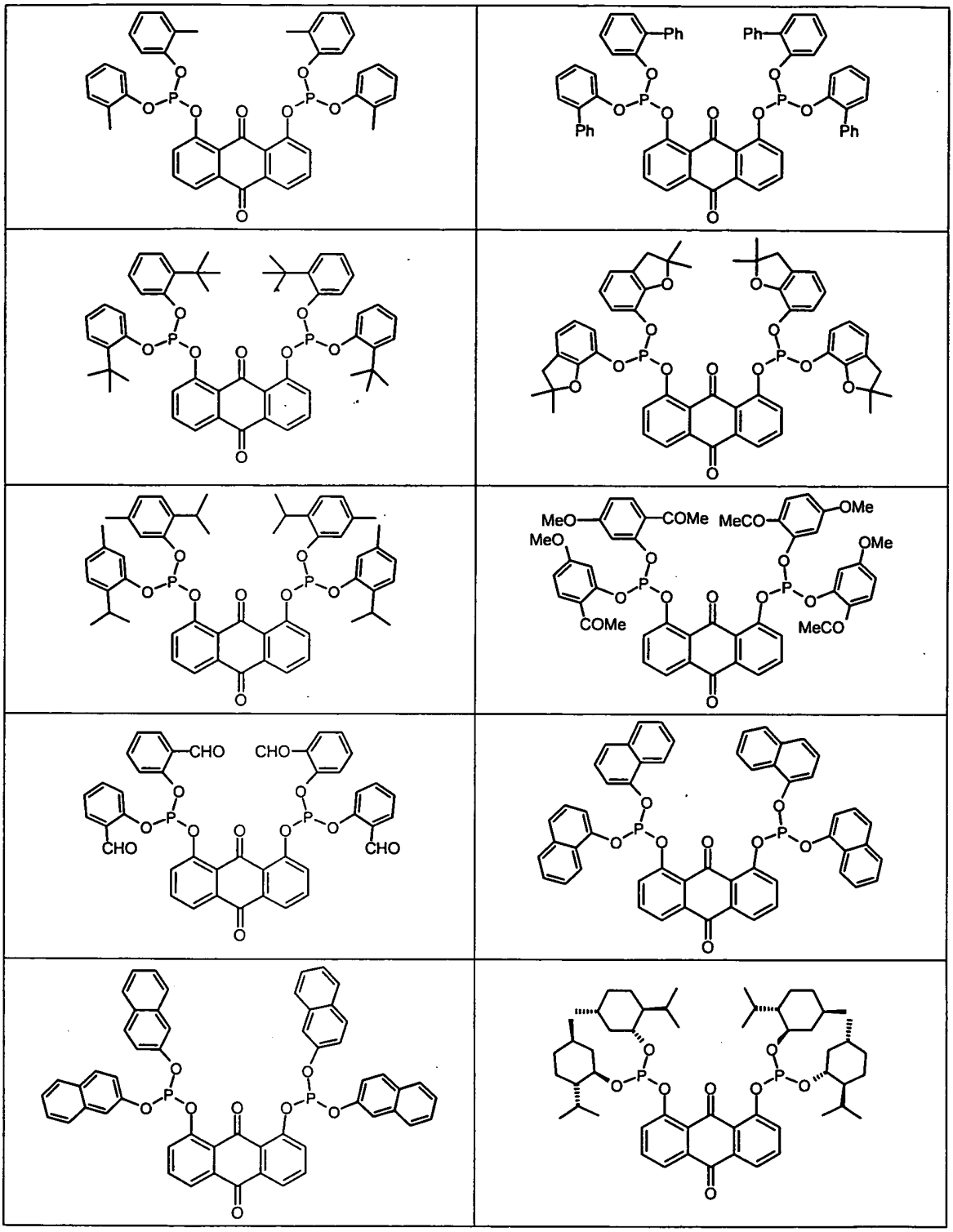
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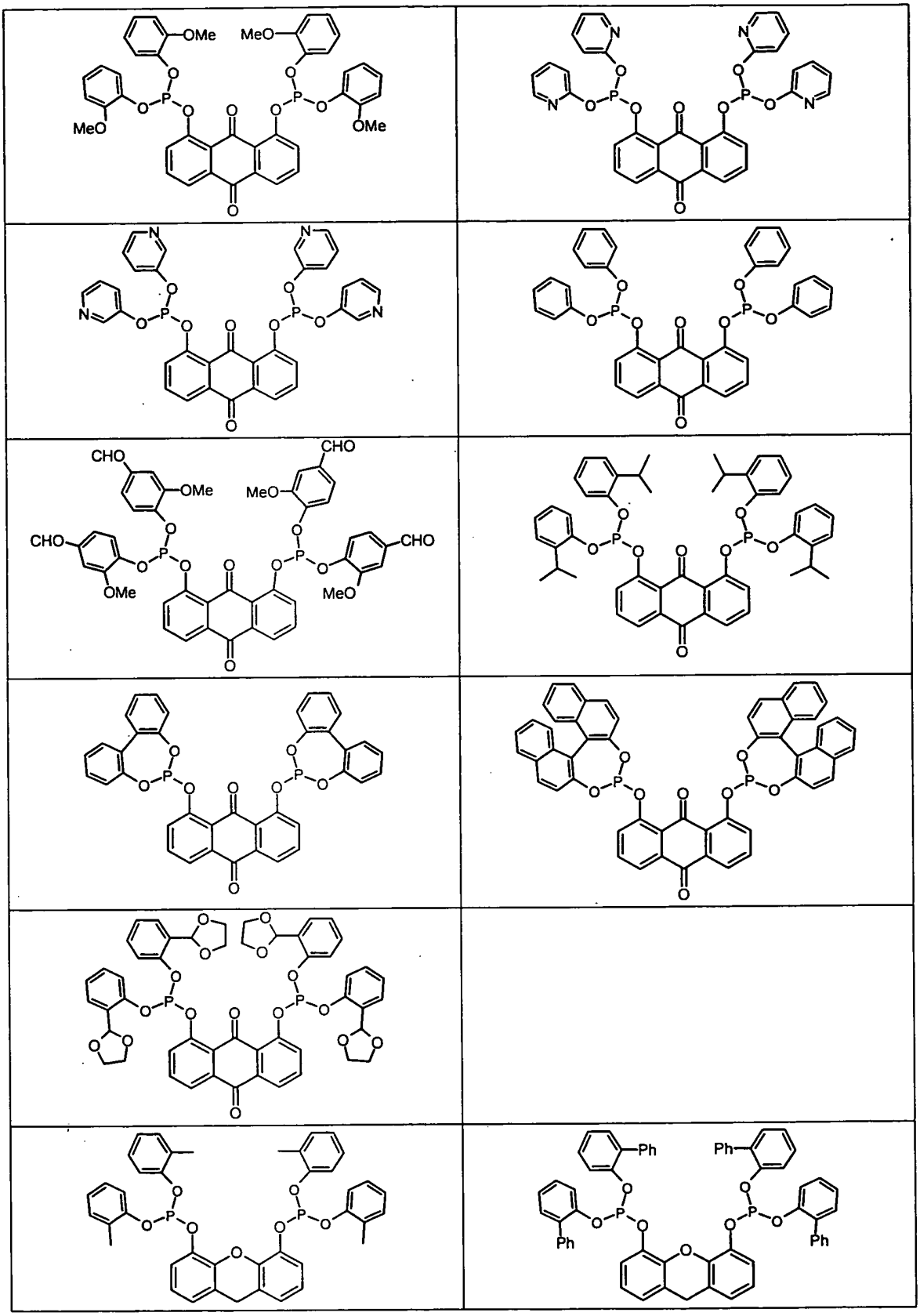

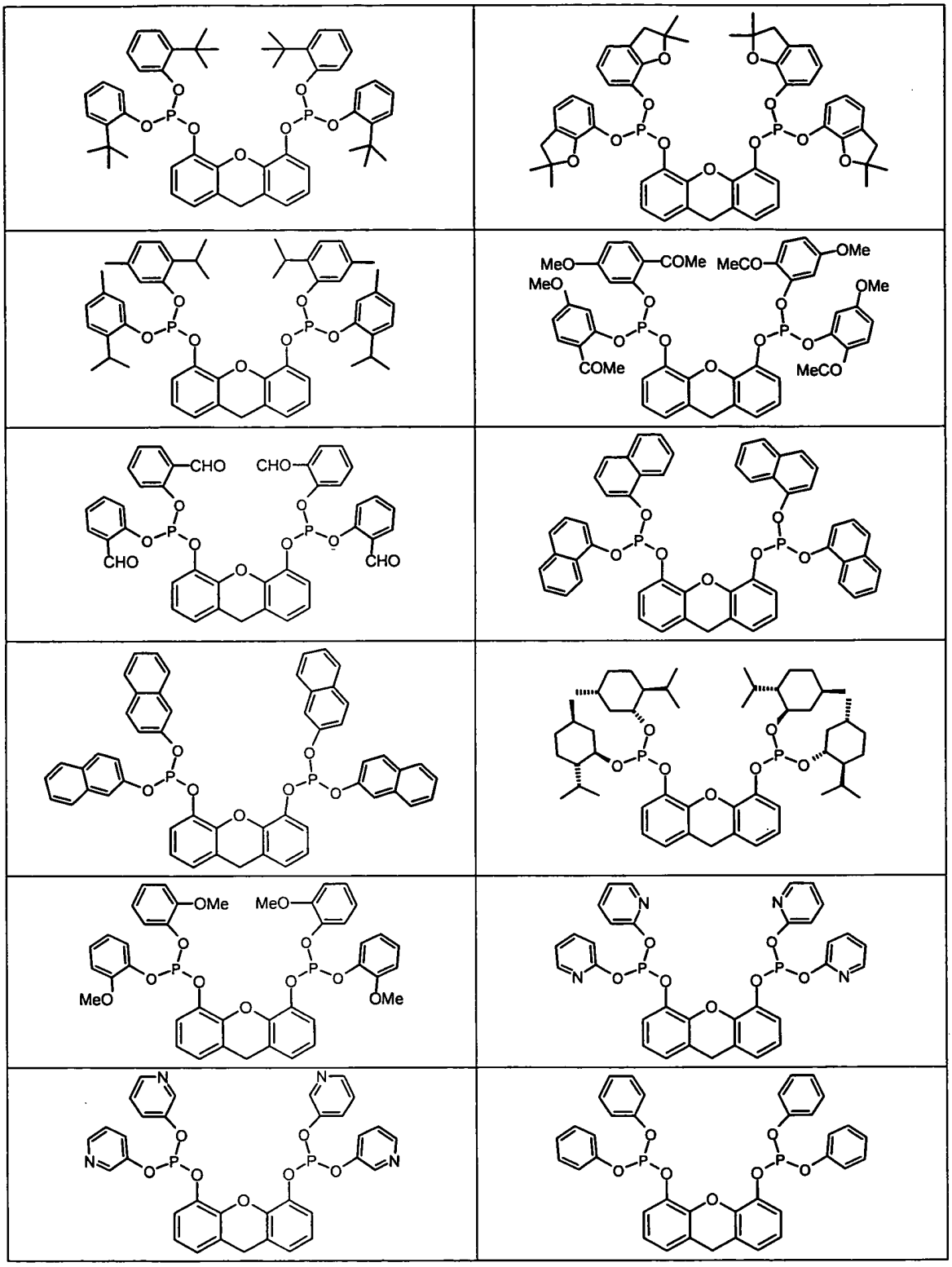
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